SYNTHESIS AND PROPERTIES OF NOVEL CAGE-FUNCTIONALIZED CROWN ETHERS AND CRYPTANDS

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A novel cryptand was synthesized which contained a 3,5-disubstituted-4-oxahexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$] dodecane "cage" moiety. In alkali metal picrate extraction experiments the cryptand exhibited high avidity towards Rb^+ and Cs^+, when compared with the corresponding model compound. A computational study of a series of cage-functionalized cryptands and their alkali metal-complexes was performed.

The X-ray crystal structure of a K^+-complexed bis-cage-annulated 20-crown-6 was obtained. The associated picrate anion was found to be intimately involved in stabilization of the host-guest complex. The interaction energy between the host-guest complex and picrate anion has been calculated, and the energy thereby obtained has been corrected for basis set superposition error.

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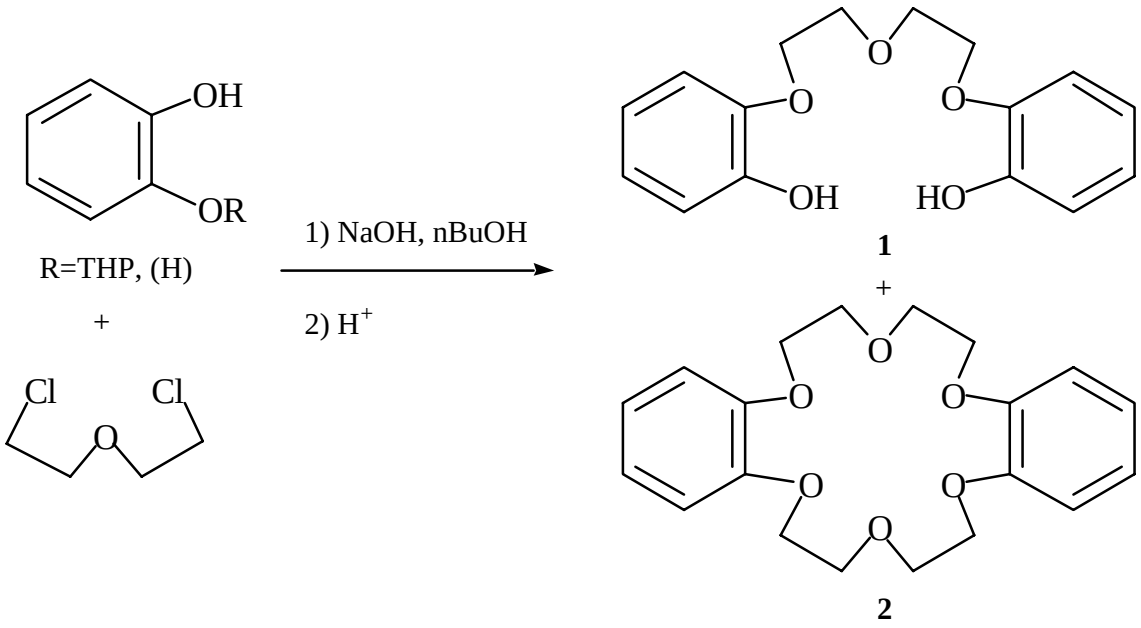
CHAPTER ONE

INTRODUCTION

In 1987, Charles J. Pedersen, Jean-Marie Lehn and Donald J. Cram were jointly awarded the Nobel Prize in chemistry for their contributions to the development and use of supramolecular chemistry.[1] Pedersen serendipitously discovered dibenzo 18-crown-6 as a byproduct of a reaction in which he had sought to obtain bis[2-(*o*-hydroxy-phenoxy)ethyl] ether, **1**. (Scheme 1). While trying to purify his product, he isolated a small amount of a white crystalline solid. Further analysis showed no alcohol groups to be present, and more interestingly, its UV spectrum changed significantly in the presence of sodium hydroxide. The unknown byproduct was identified as dibenzo-18-crown-6, **2**. Although this was not the first cyclic polyether to be reported in the literature, Pedersen was the first to recognize the unique properties of this type of compound, thereby opening up a whole new field of host-guest chemistry.[2]

Shortly after this discovery Lehn[3] adapted Pedersen's approach to incorporate macropolycyclic ligands within three-dimensional cavities, as in cryptands. Subsequently, Cram developed the concept of selective complexation by designing host systems that are capable of chiral recognition[4] and also by synthesizing molecules that mimic naturally occurring enzymes such as chymotrypsin.[1]



Scheme 1. Pedersen's reaction.[5]

Supramolecular chemistry, also known as host-guest chemistry, is concerned with the chemistry of organic complexing agents that involve non-covalent intermolecular interactions. The guest is complexed through electrostatic forces, e.g., hydrogen bonding and van der Waals interactions. Although these forces are weak individually, their cumulative effect can be significant. The weakness of the intermolecular forces can also be beneficial in that complex formation frequently is reversible.

Cyclic polyethers such as the one discovered by Pedersen consist of polyethylene glycol derivatives in a cyclic array wherein the heteroatom, most commonly oxygen, is directed toward the center of the cavity. The hydrocarbon backbone is located on the periphery of the ring, thereby rendering the cyclic polyether 'hydrophobic' on the outside and 'hydrophilic' on the inside. The heteroatoms, through their lone electron pairs are able to complex metal cations, in particular the alkali metals (Group I) and alkaline earth

metals (Group II). Pedersen envisioned that the cyclic polyethers “crown” the cations; hence, the origin of the common name for these types of compounds: *crown ethers*.

Since Pedersen's discovery in 1967, many scientists and research groups have synthesized crown ethers and have investigated the properties of many more examples of this class of compounds that serve as hosts for cations,[6] anions[7,8] and some neutral molecules.[8] This review focuses primarily on cation complexation, since this is the area most thoroughly investigated in the literature to date[9] and also constitutes the major focus of my research. A brief overview of the nomenclature used for these compounds follows.

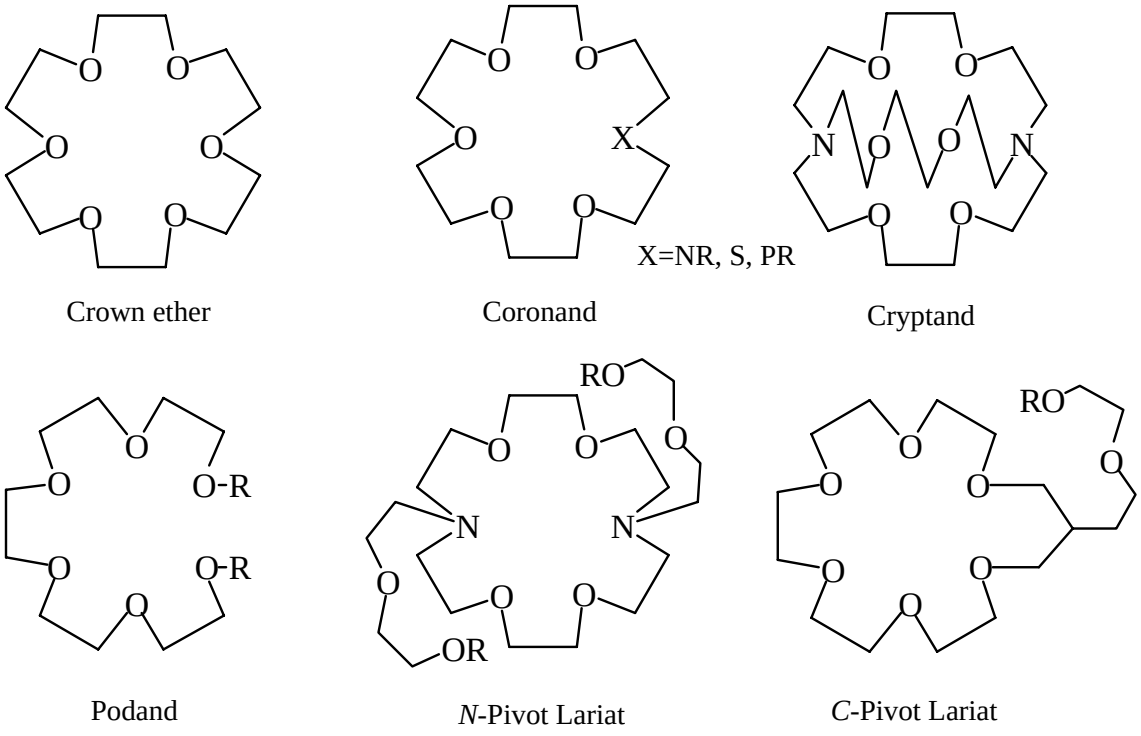


Figure 1. Nomenclature

Coronands - These are the most commonly known cyclic arrays. When all the heteroatoms in the coronand are oxygen, then the term “crown ether” is more generally used. However many modifications to the standard ethylene spacers between oxygen

heteroatoms have been made. These modifications often vary the ring size and the geometric arrangement of the heteroatoms. In addition, heteroatoms themselves can be varied, and various functional groups such as esters and amides can be introduced to influence the complexation properties of the resulting host molecule.

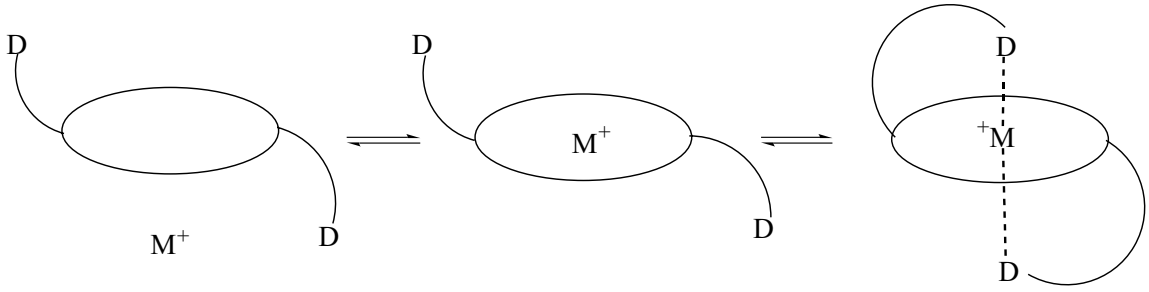
IUPAC nomenclature for polyoxamacrocyclic compounds is generally cumbersome. In practice a common naming system often is employed, which is based upon the total number of atoms in the cyclic array and the number of heteroatoms. Thus, the crown ether shown in Figure 1 is referred to commonly as "18-crown-6"; its cyclic array consists of 18 atoms, 6 of which are oxygen atoms. Coronands that contain nitrogen and sulfur are most commonly named as aza and thia-crown ethers, respectively.

Cryptands – Conventionally, cryptands contain two bridgehead nitrogen atoms that are joined by three oligooxa chains of varying length. This results in a spherical cavity in which the guest ion or molecule can be trapped. Cryptands are commonly named by the number of heteroatoms in each oligooxa chain. Hence, the cryptand shown in Figure 1 is referred to commonly as "[2.2.2] cryptand", because it consists of three linking chains, each of which contains two oxygen atoms.

Podands – These are the open-chain equivalents of coronands. The polyether chain can be rigidified into a more preorganized conformation by using more-or-less rigid donor terminal groups that employ the 'end-group' concept[10] in an effort to achieve better complexation properties.

Lariat Ethers – Lariat ethers are coronands that contain one or more sidearms attached at either C or N pivot atoms. The sidearms normally will be oligooxa chains which may contribute to the complexation process. (Scheme 2). Lariat ethers combine the

dynamic abilities of crown ethers with the capability of cryptands to envelop a guest three-dimensionally.[11]



Scheme 2. Complexation process for lariat ethers.[11]

Other more complex systems such as macropolycyclic polyethers[12] and the highly preorganized spherands[13] have also been investigated but will not be discussed here.

Properties of Host Compounds

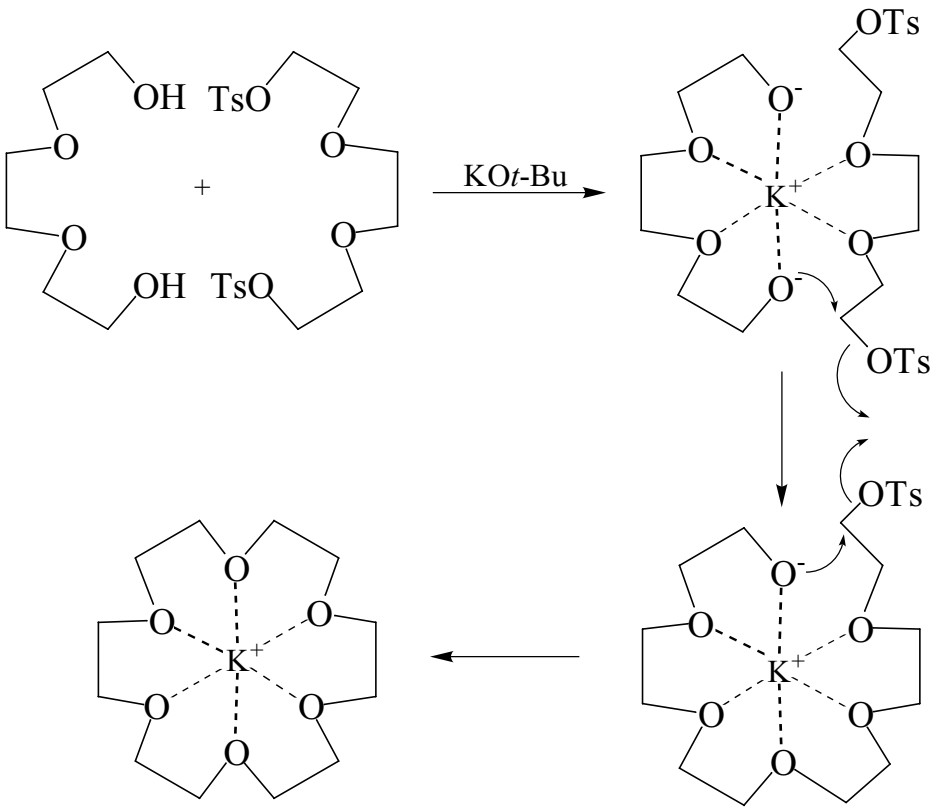
The efficiency and selectivity with which these compounds can complex a cation relies on a number of factors; e.g.; (i) shape and preorganization within the host molecule, (ii) the size-match of the host cavity to the guest,[14] (iii) cation charge and type, and (iv) donor atom charge and type. Each of these factors is discussed in more detail below.

Preorganization

The principle of preorganization states that host-guest binding is strongest when only very small changes in organization of host, guest and solvent are required for complexation.[15] Alkali metal cations are spherical; therefore, they prefer a spherical donor atom array in the host compound. In order to achieve this geometry some degree of preorganization in the host molecule is required. As is the case with most cryptands, the

relatively rigid structure of the molecule limits conformational changes, thereby effectively holding the cavity and the donor atoms in the desired spherical array.[16] Coronands possess a higher degree of flexibility within the molecule than cryptands, and some larger crown ethers have been found to adopt a collapsed conformation.[17,18] Functional groups can be incorporated into coronands which help to organize the host into the preferred conformation for complexation with a particular guest species and often, the incoming guest itself also influences the conformational dynamics of the host.

Cation influenced organization is evident in the 'template effect', a phenomenon which often is exploited during coronand synthesis. Host-guest coordination occurs via interaction between the cation and the donor atoms in the host (in this case oxygen, see Scheme 3). The cation effectively coordinates to Lewis-base sites in the ligand, thereby organizing the reactive sites into a favorable position to form the macrocycle rather than to form a linear polycondensation product. The template effect was confirmed for the example shown in Scheme 3 by using $(n\text{Bu})_4\text{N}^+$ OH^- as a base rather than KO*t*-Bu; the former base produced linear polycondensation products at the expense of the macrocyle.[19]



Scheme 3. The template effect.[19]

Size-Fit

Pedersen first suggested the "size-fit" principle in his seminal 1968 paper.[14] He found that the crown-4 hosts selectively bind Li^+, crown-5 hosts selectively bind Na^+, and crown-6 systems complex selectively with K^+. He concluded that these results reflect the relative size of each cation *vis a vis* the size and shape of the host cavity, in each case. (Table 1 and 2).

Table 1. Group I and II metal cation diameters[2]

Group I	**Ionic Diameter (A)**	**Group I**	**Ionic Diameter (A)**
Li	1.20	Be	0.62
Na	1.90	Mg	1.30
K	2.66	Ca	1.98
Rb	2.96	Sr	2.26
Cs	3.34	Ba	2.70

Table 2. Host cavity sizes of some crown ethers and cryptands.

Crown Ethers	**Cavity Diameter (A)[20]**	**Cryptands**	**Cavity Diameter (A)[16]**
14-crown-4	1.2-1.5	[1.1.1] cryptand	1.0
15-crown-5	1.7-2.2	[2.1.1] cryptand	1.6
18-crown-6	2.6-3.2	[2.2.1] cryptand	2.2
21-crown-7	3.4-4.3	[2.2.2] cryptand	2.8
		[3.3.2] cryptand	4.2
		[3.3.3] cryptand	4.8

This principle has been found to be particularly applicable to cryptands, which possess relatively rigid, three-dimensional structures. The thermodynamic stabilities of cryptand complexes (i.e., cryptates) are highly dependent upon the correlation between cation size and cavity size. The largest stability constants are seen for complexes with ions that

approach but do not exceed the size of the host cavity, i.e., [2.1.1] cryptand for Li^+, [2.2.1] cryptand for Na^+, and [2.2.2] cryptand for K^+. The larger cryptand cavities [3.2.2] and [3.3.3] less closely match the size of any of the alkali metal cations as evidenced by a corresponding reduction in complexation specificity.[16]

The size-fit principle does have its limitations; cations too large or too small to fit within a cavity may still be complexed but not necessarily completely within the cavity or on a 1:1 host:guest basis. More complex host-guest relationships are known, for example 2:1 "sandwich-type" complexes. In such cases, other factors such as cation charge and type, ligand donor atom type, ligand substituents and solvent become important.[21]

Donor atom selection

Pearson's hard-soft acid-base (HSAB) principle[22] provides a useful starting point for donor atom selection when designing a host for a particular guest. The principle states that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases, where hard acids have small highly charged and nonpolarisable acceptor atoms and soft acids are larger and not so highly charged. Correspondingly hard bases have small, highly electronegative donor atoms and soft bases are larger and more polarisable.[23] The bonding between hard acids and hard bases is dominated by electrostatic interactions, whereas the bonding between soft acids and soft bases is primarily covalent in nature. Crown ethers utilizing ether oxygens as donor atoms, which are "hard base" species, coordinate well with the hard acid, alkali metal cations.

Substitution of various heteroatoms for oxygen in the crown ether has been investigated; modifications of this type are known to affect the complexing abilities of the host compound. The most common heteroatoms thus employed are N and S. Although in coordination chemistry neutral nitrogen donors are known to display stronger coordinating properties with many metals than neutral oxygen donors,[24] substitution of a N atom for an O atom in crown ethers frequently results in reduced complex stability, probably due to the fact that the van der Waals radius of N is larger than that of O, and the resulting molecular dipole moment is smaller. Substitution of O by a pyridine N, generally results in reduced complex stability with alkali metals.[21]

Substitution of O by a S atom also results in decreased stability of complexes with alkali metal cations. However, this substitution frequently results[6] in a considerable increase in the stability of complexes with Ag^{+} and Hg^{2+} as would be expected based upon consideration of the hard-soft acid-base principle.[22] Sulfur is a soft base and therefore is expected to interact more strongly with soft acids.

An interesting factor in these complexes is that they tend to display 1:2 cation:ligand stoichiometry. If the donor atoms were pointed inwards toward the center of the cavity, the larger size of the sulfur atoms would result in reduced cavity size. However, it has been found that in most cases, the sulfur atoms are directed outwards away from the cavity, which accounts for the fact that thia host compounds tend not to form inclusion complexes.[25] Recently, evidence was obtained[26] by X-ray crystal structure for a tetra-thia cryptand which does form an inclusion complex with Hg^{2+}.

Functional groups also have been incorporated into host compounds in an effort to modify their complexation properties. Benzo substituent groups (see compound **2**, Scheme 1) reduce the binding strength and selectivity of coronands and cryptands.[16] There are a number of reasons thought to be responsible for this:

(i) The O-O distance is smaller between the two oxygens joined by the benzene ring than those connected by an ethylene unit, thereby resulting in reduced cavity size.

(ii) The benzene ring also is electron withdrawing, thereby reducing the electron density and basicity of the adjacent oxygen atoms.

(iii) Benzo groups provide a rigid component that reduces the overall flexibility of the crown ether.

Esters and amides are other examples of functional groups that have been incorporated into host compounds;[9] they display affinity for complexation with alkaline earth metals Ca^{2+} and Sr^{2+}. These groups have a stronger dipole than the ether linkages. However, it is in the wrong direction, i.e., negative charge is directed away from the cavity; hence in most cases other than those mentioned above, this functionality tends to result in reduced binding ability.

Alkyl chains and polycylic moieties have been incorporated to increase the lipophilicity of the host. Applications of crown ethers and like compounds to solvent extraction and membrane transfer require that the host ligand be completely soluble and maintained permanently in the organic phase.[27]

Crown ethers have also been used successfully for chiral recognition. Incorporation of optically active moieties into the crown ether frequently enables it to bind selectively to one enantiomer, thereby potentially providing a technique for optical resolution. In their 1997 review article,[28] Zhang, Bradshaw, and Reed presented a set of empirical rules that might be used for the design of effective new chiral macrocycles:

(i) the chiral macrocycle must form reasonably stable complexes with the guest enantiomers,

(ii) large chiral barriers result in a high degree of enantiomeric recognition

(ii) low conformational flexibility of the complexes is important for good enantiomeric recognition,

(iii) structural complementarity between the chiral macrocycles and the guest enantiomers is important in order to form stable complexes and to make full use of repulsive interactions between chiral substituents and

(iv) macrocycles containing C_2, C_3 and D_2 symmetry tend to show higher enantioselectivity than those of C_1 and D_3 symmetry.

The binapthyl containing crown ether shown in Figure 2 was shown to resolve racemic phenylglycine methyl ester ammonium salts.[5]

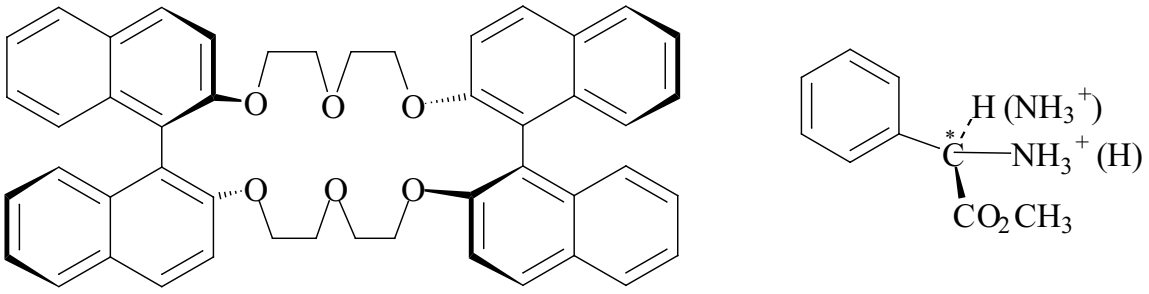


Figure 2. A chiral crown ether with C_2 symmetry.[5]

Extraction Ability

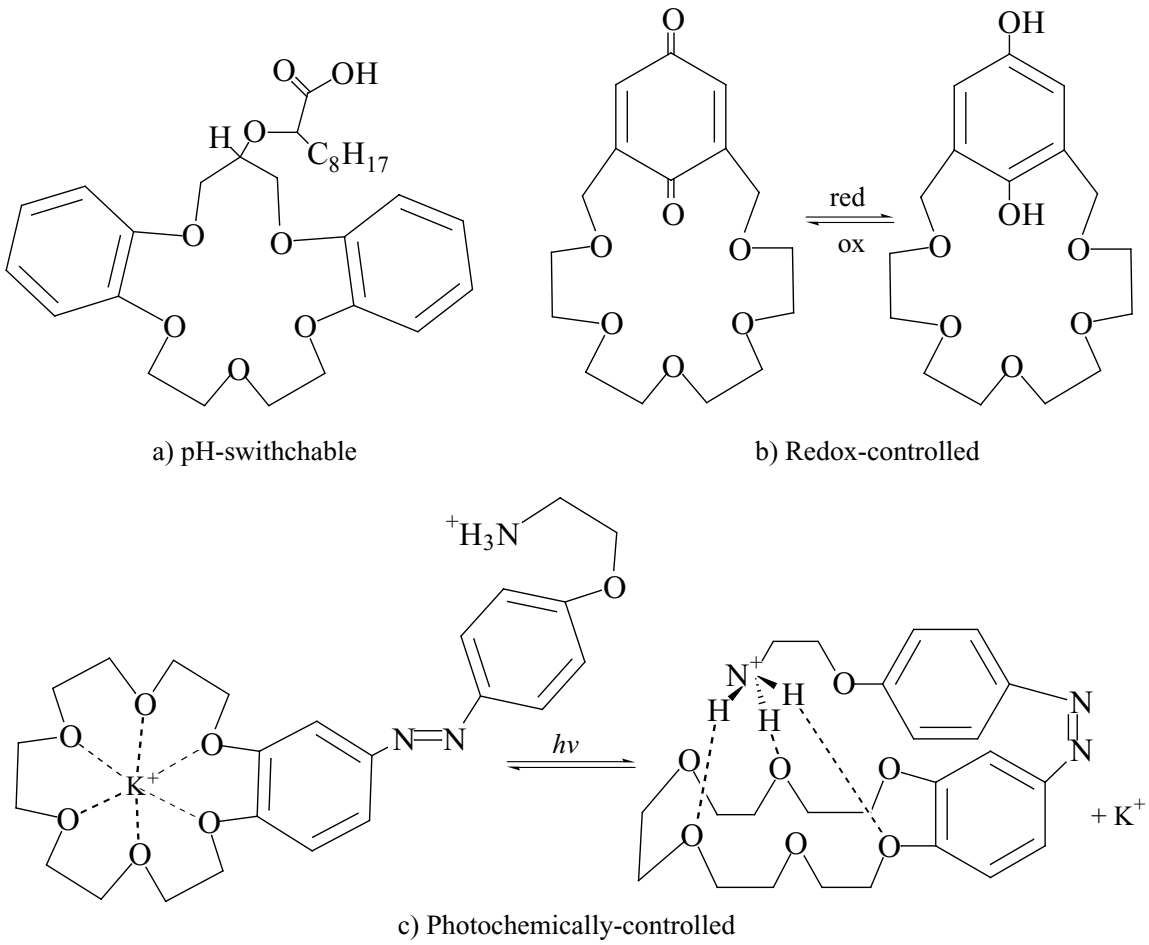
The ability of a given host molecule to form strong complexes with cations clearly is an important contributing factor that determines overall extraction ability. Those ligands that bind cations can be divided into two categories; cation carriers and cation receptors. Crown ethers tend to fall into the former category, since they form complexes that are fairly strong but are sufficiently dynamic to permit the cation to be released in the reverse process. Cryptands belong to the latter cation receptor category. They form very strong complexes that resist recovery of the metal cation guest via solvent stripping.

$$M^+_{solv} + Ligand_{solv} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\, M^+ \; Ligand \,]_{solv}$$

$$K_s = \frac{k_1}{k_{-1}} \qquad \textbf{Equation 1}$$

Equation 1 defines the stability constant K_s for ligand-cation complexation. In most applications of solvent extraction, the cation is extracted from one liquid phase (aqueous source phase), transported through a hydrophobic membrane, and then deposited into an aqueous receiving phase. This process demands that the cation carrier possess different properties in the different phases.[11] In the source phase, binding should be strong and rapid, so both K_s and k_1 should be large. When passing through the hydrophobic membrane the cation needs to remain bound strongly, so K_s must again be large. Finally the cation must be released into the receiving phase; therefore K_s should now be small and k_{-1} large. In most cases, this presents a paradox, and requires some compromise between host-guest binding strength and ligand dynamics.

More recently, host compounds have been designed that can be switched "on" or "off", thereby manifesting either strong or weak binding ability, respectively. These switchable crown ethers can be pH-, redox-, and/or photochemically-controlled.[15,27] (Figure 3).



a) pH-swithchable

b) Redox-controlled

c) Photochemically-controlled

Figure 3. Switchable crown ethers[27]

Applications

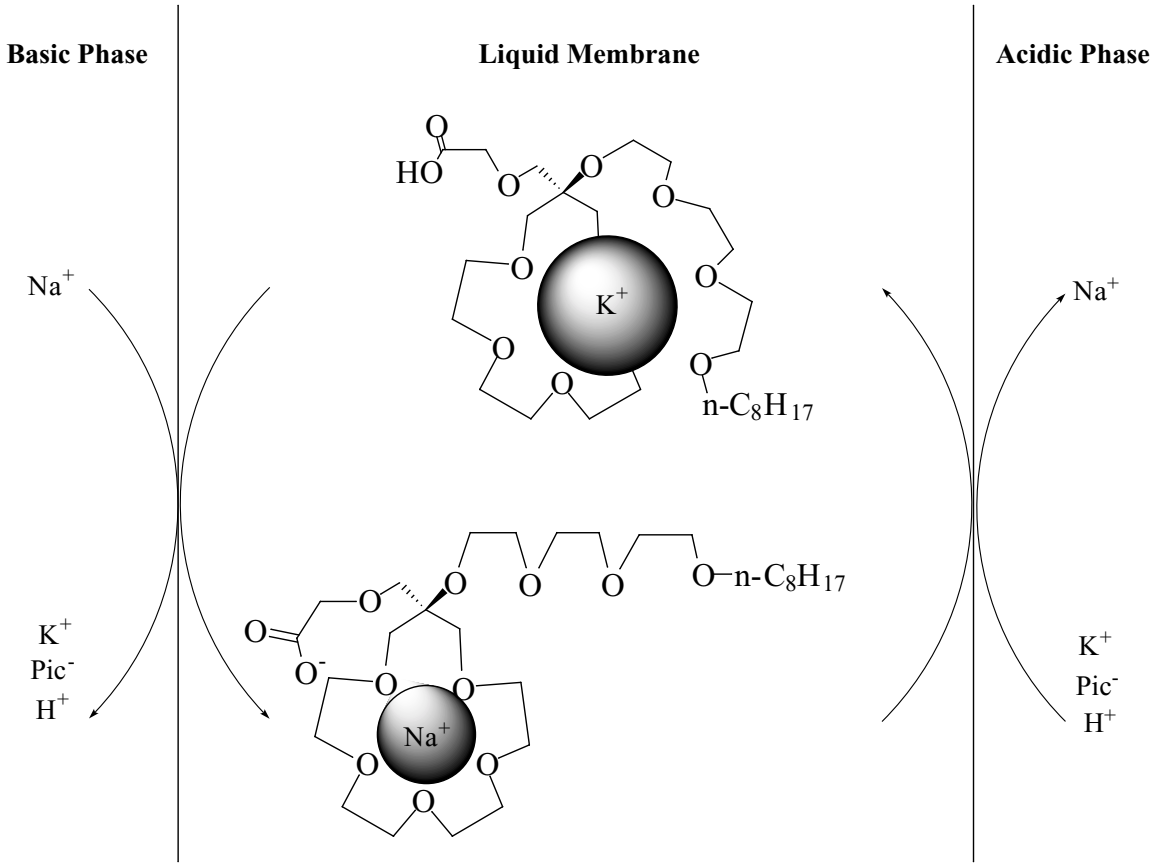
The ability of crown ethers to complex cations has found application in a wide range of fields, e.g., phase transfer catalysis (PTC), extraction of alkali metal, alkaline

earth metal and heavy metal cations, transfer of ions across membranes, and chiral recognition.

PTC is a technique used when the reagents required for a reaction are not soluble in any one solvent system. The basic premise is that a phase transfer catalyst can be selected which can transport one of the reactants into the reaction phase of the other reactant and thereby maintain a high reaction rate.[29] For industrial applications, there are a number of criteria that must be considered when selecting a phase transfer catalyst, such as catalytic ability, stability, separability, toxicity and cost.[30] Quaternary ammonium salts tend to be used whenever possible, because they are significantly cheaper; however, in many cases, crown ethers are used for this purpose due to their thermal stability. Dibenzo 18-crown-6 is a typical example of the crown ethers that are employed for reactions which involve K^+.

In phase transfer reactions, crown ethers and cryptands work in two capacities, i.e., organic "masking" of the cation and anion activation.[31] The alkali metal cation is complexed by the crown ether, thereby enabling it to be extracted or solubilized with the accompanying anion into non-polar organic solvents. By thus masking the cation, the anion is effectively released from the ion pair, thereby increasing its reactivity as a nucleophile or base.

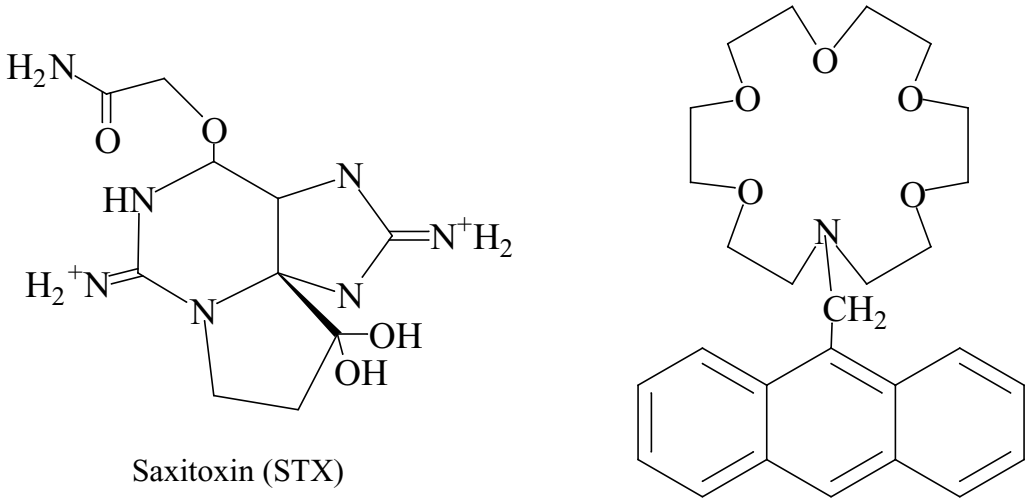
The principles involved in this process appear to be straightforward; however, Knochel and coworkers[32] concluded that there is no simple correlation between the extent of solubilization of the ion pair and reaction rate. After investigating various crown ethers, podands and cryptands, they suggested that other factors such as the stability of the complex formed and lipophlicity and rigidity of the ligand also must be considered.



Scheme 4. A pH responsive countercurrent double uphill transport system.[33]

Scheme 4 illustrates the use of a pH-responsive crown ether designed by Ikeda and co-workers[33] which is able to transport two different cations in opposite directions against their concentration gradients. This is an interesting model for the cation transport system of a cell. Sodium cation is transported from the basic phase into the acidic phase as the counterion of the carboxylate anion. The crown ether facilitates the transfer through the liquid membrane by coordinating with Na^+. In the opposite direction, K^+ is transported from the acidic into the basic phase. The electron donating oxygen atoms from the lariat arm help to coordinate the ion, since K^+ is too large to be included within the 16-crown-5 cavity.

Crown ethers also have been used in chemical sensors. A specific example of this is in fluorescence sensors of saxitoxin (STX), a bis-guanidium ion.[34] (Figure 4). A crown ether known to bind STX is covalently attached to a fluorophore (e.g. anthracene). In the presence of STX, a 20-30 fold enhancement in fluorescence intensity was achieved. These sensors can be used to detect increases in STX, which is produced by dinoflagellates, bacteria and blue and green algae near shellfish beds. This is known to be the cause of paralytic shellfish poisoning, which can be fatal.



Saxitoxin (STX)

Figure 4. A sensor for saxitoxin.[34]

Crown ethers also have been used in medical applications as diagnostic aids when incorporated into selective electrodes and as therapeutic agents that help to rid the body of toxins.[27]

CHAPTER TWO

SYNTHESIS AND ALKALI METAL PICRATE EXTRACTIONS OF A CAGE-FUNCTIONALIZED CRYPTAND

Introduction

Of critical importance in the use of crown ethers, cryptands and other host molecules for solvent extraction and liquid membrane transport is the issue of solubility in the organic phase.[27,35] If the host is not completely soluble in the hydrophobic organic phase, loss to the aqueous phase will occur, thereby resulting in the reduced efficiency of the extraction or transport process and reduced recovery of the naked host ligand. Other important considerations include; (i) conformational flexibility, which will affect the ability of the host to form a host-guest complex and subsequently to release the guest, and (ii) molecular weight, which will affect mobility.[35]

Often, these various factors work against each other; for example long-chain alkyl groups have been incorporated into the host molecule to increase lipophilicity. However, the concomitant increase in molecular weight results generally in a corresponding loss of mobility. Kimura and coworkers[36] incorporated long-chain alkyl groups to their advantage when designing a Li^+-selective 14-crown-4 derivative. (Figure 5). Although 14-crown-4 is known to have remarkable selectivity for Li^+ due to the close match between cation and host cavity sizes, 2:1 (host: cation) “sandwich-type” complexes with Na^+ and K^+ also are formed readily. Incorporation of bulky substituents such as dodecyl

and benzyl groups affects both the mobility and the conformational flexibility of the host system to the extent that 2:1 complexes no longer are formed without concomitant reduction in avidity for Li^+.

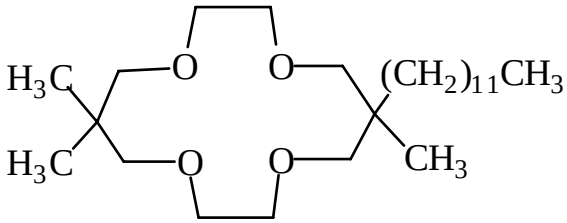
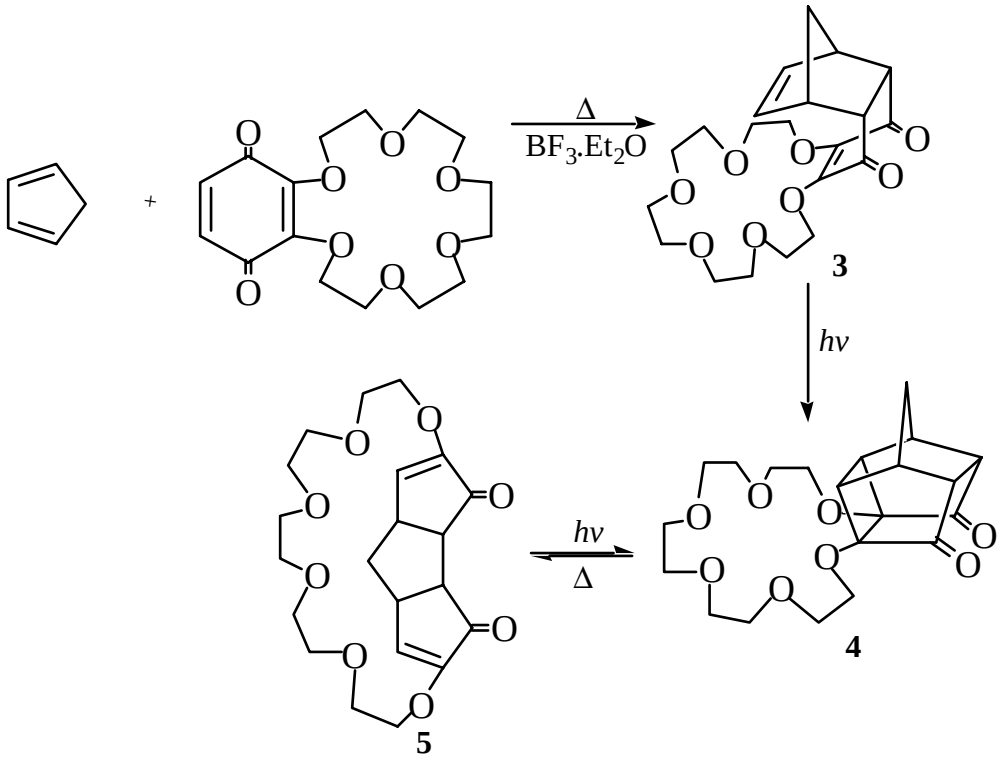


Figure 5. An example of the Li^+-selective lariat crown ethers designed by Kimura and coworkers.[36]

Other efforts to increase lipophilicity have focused upon the use of more highly rigid aliphatic moieties. The earliest example in this regard is Pedersen's dicyclohexyl-18-crown-6 and its derivatives.[2] He found that the complexes that involve these hosts display greater solubility than the other hosts tested. When placed in contact with water, most of the crown ether remains in the organic phase, although the guest cation and its counter anion are transferred rapidly into the aqueous phase.



Scheme 5. Crowned *p*-benzoquinones in cycloaddition reactions.[37a,b]

Kanematsu and coworkers used crowned *p*-benzoquinones as the diene in Diels-Alder reactions with cyclopentadiene.[37a,b] Subsequent photochemically-promoted intramolecular [2+2] cycloaddition converted **3** into the corresponding cage-annulated crown ether, **4**. In this case, the carbocyclic framework not only acts to increase the lipophilicity of the crown ether but also serves as a photoresponsive moiety. When heated, **4** can be converted into **5**. In the reverse process, **5** is converted into **4** via irradiation. Results of extraction experiments showed that neither **3** nor **4** display noteworthy selectivity among alkali metal cations. However, **5**, the product formed from **4** via cycloreversion, possesses a larger ring size and has been observed to be selective toward extraction of Rb^+ from aqueous solution into $CHCl_3$.[37c]

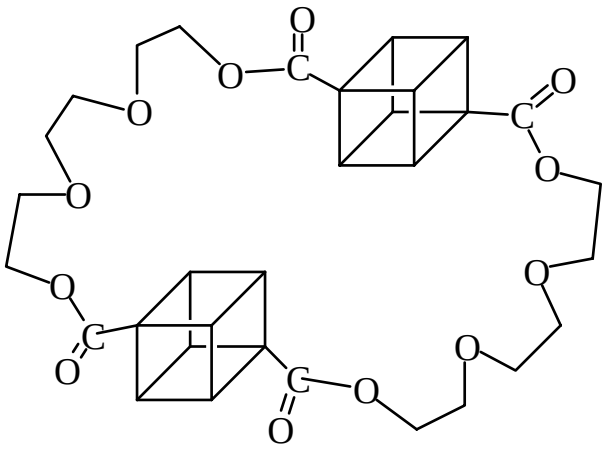


Figure 6. A crown ether containing a 1,4-bridged cubadiyl system.[35]

Moriarty and coworkers[35] synthesized crown ethers that contain one or two 1,4-bridged cubyl groups as a rigid lipophilic component. (Figure 6). They considered the C_8 moiety to be a low molecular weight lipophilic center, which serves to anchor the ionophore in the organic membrane.

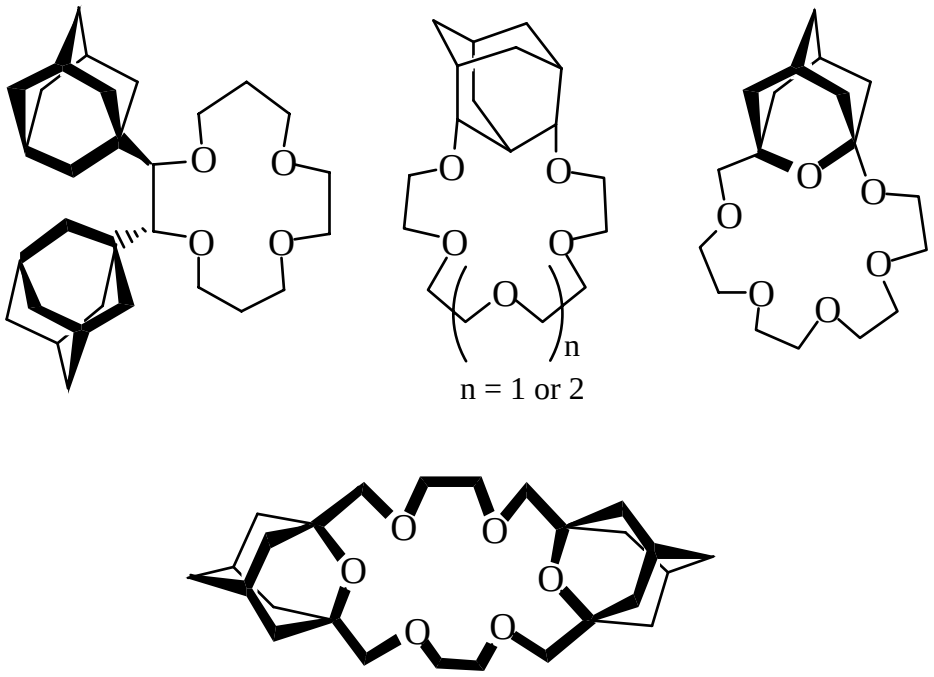
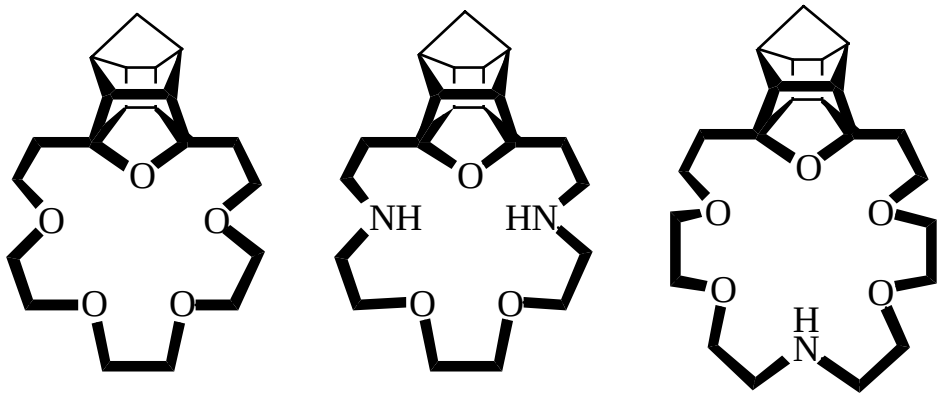


Figure 7. Crown ethers containing adamantane and oxaadamantane moieties.[38,39]

Adamantane also has been used as a rigidifying, hydrophobic moiety on numerous occasions;[38,39] some examples in this regard are shown in Figure 7. More recently, oxaadamantane moieties have been incorporated into crown ethers, thereby conferring a dual functionality upon the cage moiety, since the cage oxygen atom can also function as an additional donor atom in the crown ether.



6 **7** **8**

Figure 8. Some cage containing crown ethers.[40-42]

Research in our group has focused upon incorporation of the 3,5-disubstituted-4-oxahexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane (cage) moiety into novel crown ethers,[40-44] cryptands[43-46] and molecular boxes.[44,47] The oxahexacyclic cage unit acts as a rigidifying spacer as well as by furnishing an oxygen atom which can act as a donor site in the host. Some examples of the host systems that have been synthesized previously are shown in Figure 8. Picrate extraction experiments performed by using **6**-**8** show increased avidity toward all alkali metal picrates when compared with the results obtained for the corresponding model compounds which do not contain the cage moiety.[40-42]

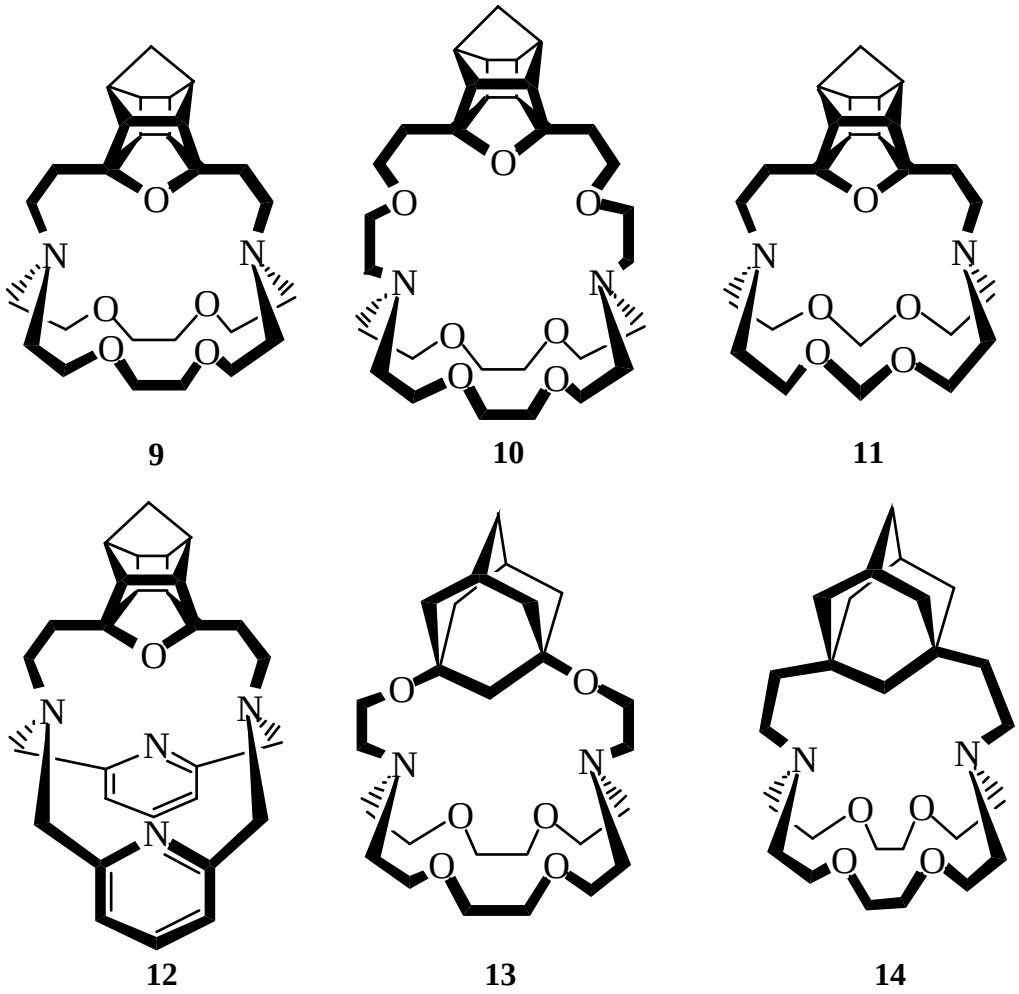


Figure 9. Cryptands containing cage moieties.[41a,43-46]

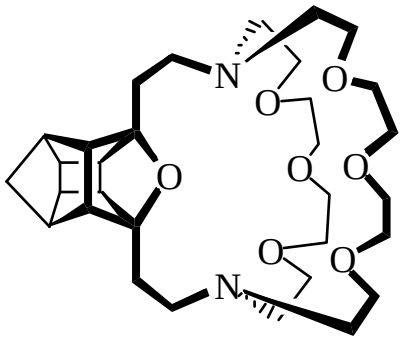
To date, relatively few cryptands that contain cage moieties have been synthesized; some of those which have been reported are shown in Figure 9. Data obtained via alkali metal picrate extractions that utilize these cage-annulated cryptands are shown in Table 3.

Table 3. Alkali metal picrate extraction data (% alkali metal picrate extracted).

Cryptand	Li^+	Na^+	K^+	Rb^+	Cs^+	Reference
9	39.8 ± 0.8	95.1 ± 0.8	89.7 ± 1.2	56.1 ± 0.1	33.7 ± 0.7	45
10	36.3 ± 0.6	50.0 ± 0.7	74.7 ± 0.8	68.4 ± 1.0	60.9 ± 0.8	41a
11	68.4 ± 0.8	61.9 ± 0.6	42.0 ± 0.3	31.6 ± 0.5	30.1 ± 0.8	46
12	81.9 ± 0.7	70.7 ± 0.8	40.3 ± 0.5	46.0 ± 0.6	40.9 ± 0.9	43
13	16.2 ± 0.6	21.9 ± 0.2	19.2 ± 0.5	21.1 ± 0.7	18.1 ± 0.6	44
14	11.2 ± 0.4	22.4 ± 0.6	46.7 ± 0.5	25.4 ± 0.7	22.1 ± 0.7	45

Cryptand **9**[45] was found to be particularly interesting; it exhibits unusually high avidity toward complexation with Na^+ and K^+. The X-ray crystal structure of the Na^+-complexed cryptand (**9**•Na^+) [45] indicates that the cation is bound to all seven Lewis base centers (two nitrogen and five oxygen atoms).

The purpose of the present research was to extend these previous studies to include a larger target host cryptand, i.e., **15** ("cage-[3.3.1] cryptand").

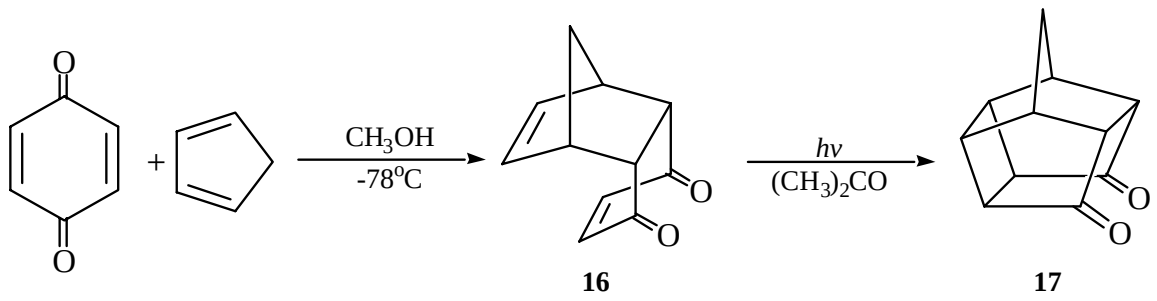


15
("cage-[3.3.1] cryptand")

It was anticipated that the increase in cavity size will result in selective complexation of larger cations, possibly Rb^+ or Cs^+.

Results and Discussion

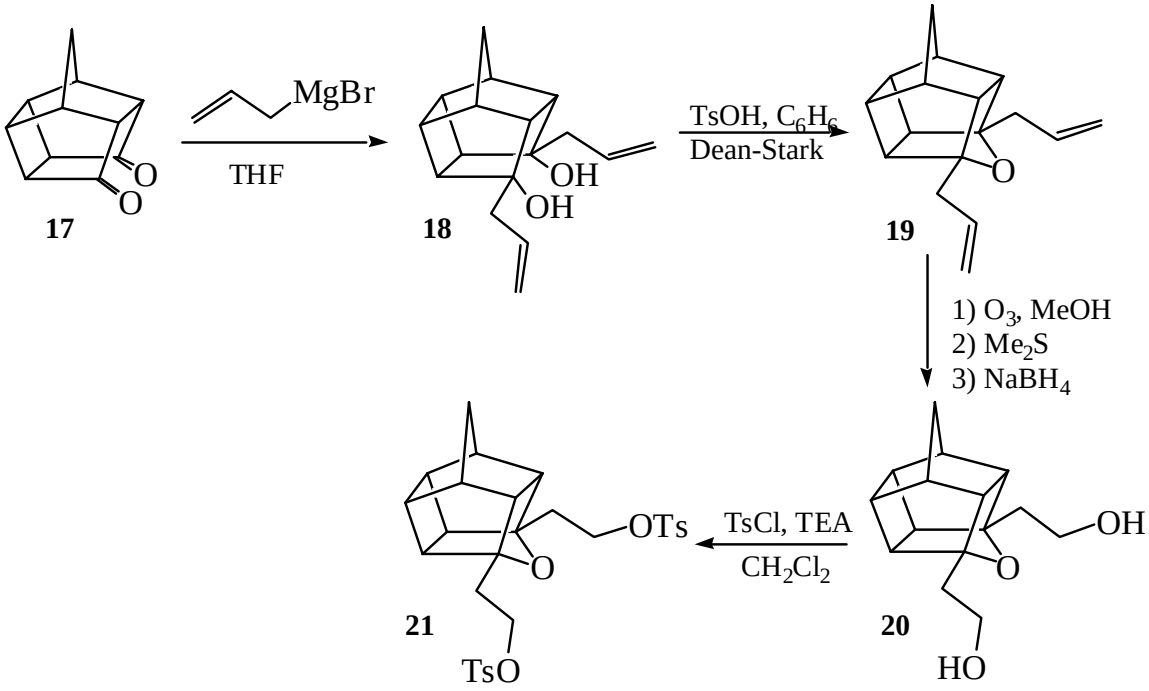
The synthetic strategy followed when preparing cage-[3.3.1] cryptand, **15**, was very similar to that previously reported for the synthesis of **9**.[45] Thus, pentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione ("PCU-8,11-dione", **17**) was synthesized, as shown in Scheme 6, by following a previously reported method.[48] Diels-Alder reaction of *p*-benzoquinone to cyclopentadiene afforded the corresponding adduct **16**.[49a] Subsequent intramolecular [2+2] photochemical cyclization of **16** produced the cage dione **17**.[49b]



Scheme 6. Synthesis of "PCU-8,11-dione".[48]

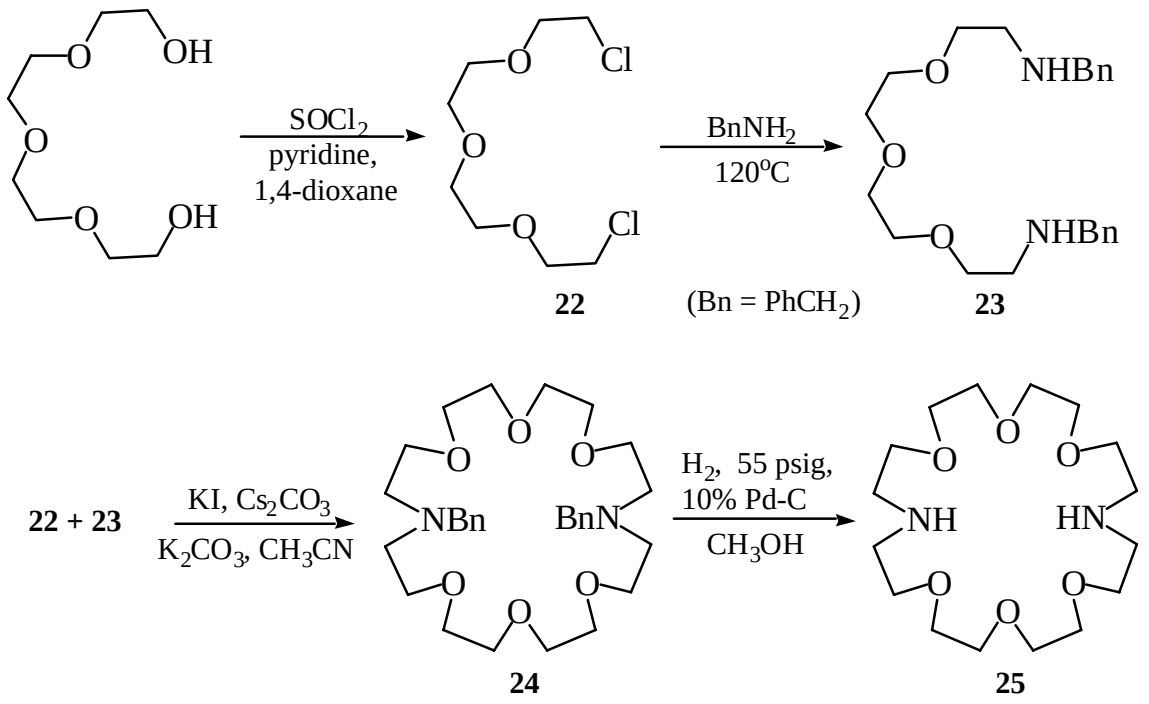
Synthesis of ditosylate **21**, used subsequently to prepare cryptand **15**, is shown in Scheme 7. Reaction of the PCU-8,11-dione, **17**, with excess allylmagnesium bromide afforded the corresponding *endo*-8, *endo*-11 diol, **18**,[41b] which subsequently was dehydrated in the presence of a catalytic amount of *p*-toluenesulfonic acid (TsOH) by removing water via azeotropic distillation in a Dean-Stark apparatus, to produce the corresponding diallyl ether, 3,5-bis(prop-2-enyl)-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]

dodecane, **19**.[41b,42] Ozonolysis of **19** followed by a reductive workup afforded the corresponding diol, **20**,[40] which could be converted readily into ditosylate **21**.[42,45]



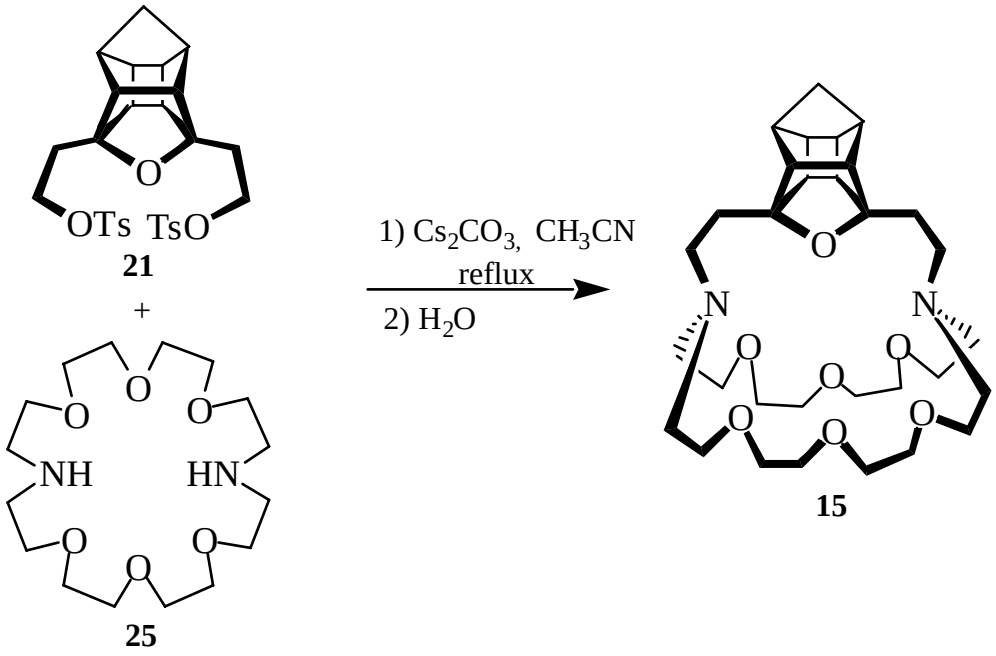
Scheme 7. Synthesis of ditosylate, **21**.

The synthetic route employed to prepare 1,13-diaza 24-crown-8, **25**, is shown in Scheme 8. Dichloride **22** was prepared by using tetraethylene glycol as previously reported.[50] Subsequently, **22** was reacted with benzylamine to afford **23** by using a modification of a previously reported method.[51] Reaction of **22** with **23** to afford **24**[52] was performed by using a mixture of Cs_2CO_3 (template) and K_2CO_3 (excess, base). Hydogenolysis of the *N*-benzyl groups in **24** yielded the corresponding diamine, **25**.[53,54]



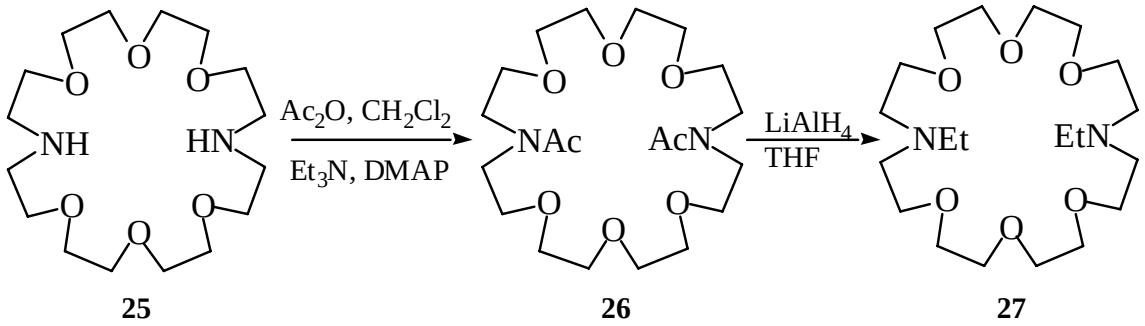
Scheme 8. Synthesis of diaza 24-crown-8, (**25**).

Coupling of **25** to **21** (Scheme 9) involves two sequential S_N2 reactions that proceed via nucleophilic attack by amine nitrogen atoms in **25** to displace the tosylate leaving groups in **21**. Both K_2CO_3 and Cs_2CO_3 were used (under high dilution conditions) in an effort to identify the more suitable templating agent. Cs_2CO_3 produced **15** in 43% yield, whereas K_2CO_3 afforded the desired product in only 35% yield. The product obtained from these reactions contains a mixture of both metal-complexed and non-complexed ligand which was difficult to separate cleanly. Accordingly, the mixture was dissolved in $CHCl_3$ and was extracted with water to remove any metal-complexed material, thereby leaving behind in the organic layer the free ligand which could be further purified by column chromatography.



Scheme 9. Synthesis of cage-[3.3.1] cryptand, **15**.

In connection with the alkali metal picrate extraction experiments, it was necessary to employ a model host compound, which lacks the cage moiety, for purposes of comparison. *N*,*N*'-Diethyl 1,13-diaza 24-crown-8, **27**, was chosen for this purpose; this model compound was prepared by using the procedure outlined in Scheme 10. Thus, **25** was *N*-acetylated to produce **26** by using an adaptation of a previously reported method.[47] Subsequent reduction of **26** with $LiAlH_4$ yielded the desired product, **27**.



Scheme 10. Synthesis of the model compound.

Compound **26** was of particular interest due to the fact that its ^{13}C NMR spectrum displays peaks that correspond to each of the individual C atoms in the crown ether ring. One possible explanation is the presence of a mixture of diastereomers that are not interconverting. However these structures would still contain symmetry elements and therefore, do not account for the number of peaks seen in the ^{13}C NMR spectrum. Thus it is thought that this result probably reflects the fact that the amide bonds prevent *N*-inversion, thereby effectively configurationally "freezing" the amide bonds into a non-symmetrical alignment.

The single crystal X-ray structure of **26** was obtained[18] (Figure 10), which indicates that the structure possesses inversion symmetry. The crown ring lies in an approximate plane with the acetyl groups approximately orthogonal to the plane.[18] Apparently the symmetry observed in the solid phase is lost when the compound is placed in solution, wherein additional conformational flexibility is possible.

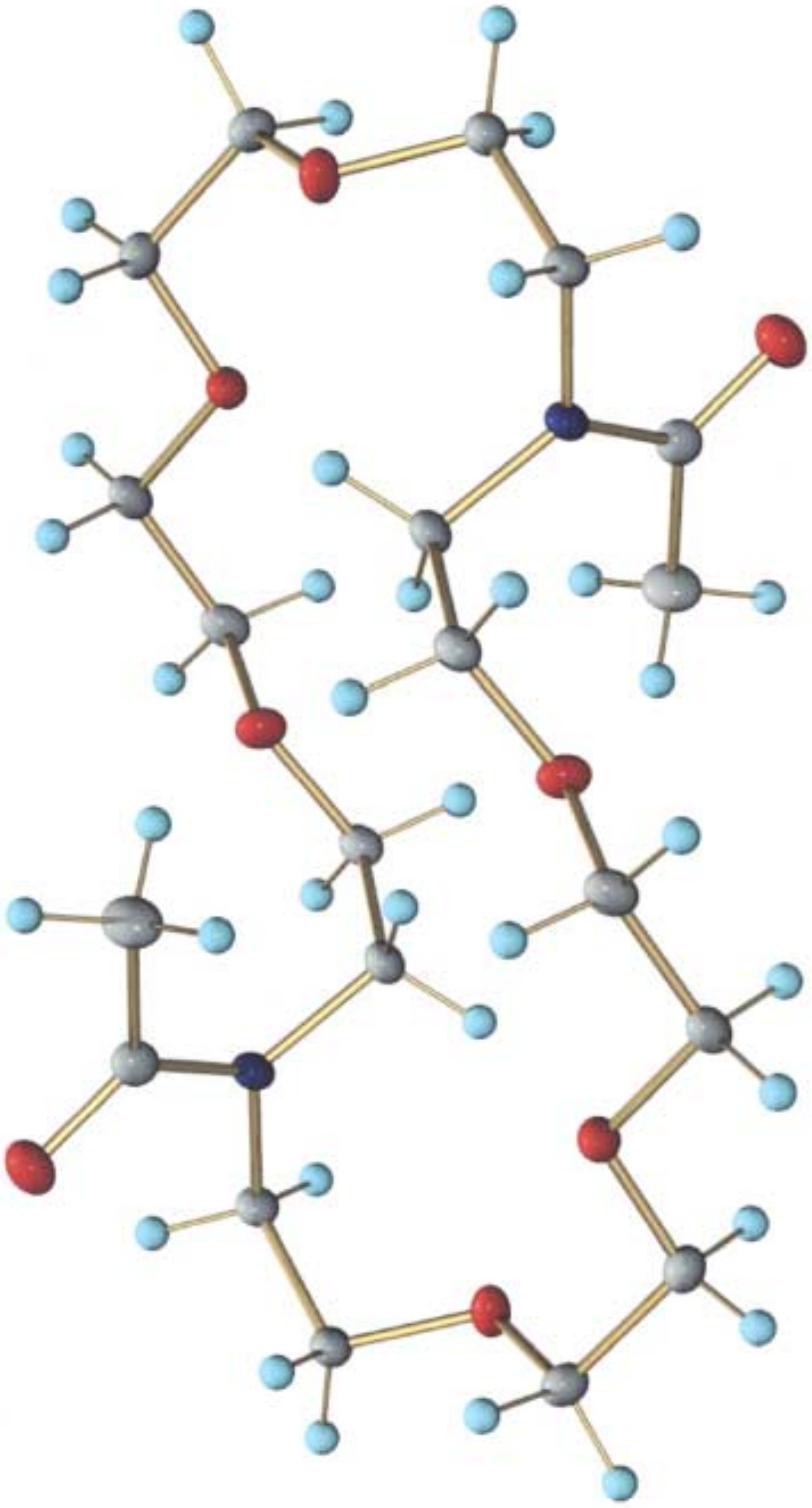
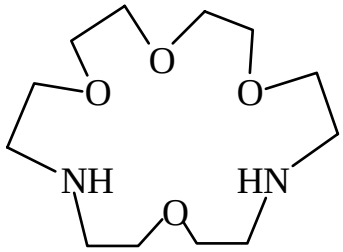


Figure 10. X-ray structure drawing of *N,N'*-Diacetyl-1,13-diaza-24-crown-8 (**26**).[18]

Alkali Metal Picrate Extraction Experiments

Alkali metal picrate extraction experiments[55] were carried out to assess the extraction ability of **15** in comparison to that of the corresponding model compound, **27**. In these experiments the amounts of alkali metal picrate salts extracted from the aqueous phase into the organic phase in the presence of the host compound were measured spectroscopically. The equilibrium thereby established is shown in equation 2.

$$M^+_{(aq)} + Pic^-_{(aq)} + C_{(org)} \rightleftharpoons [M^+ C\ Pic^-]_{(org)} \qquad \textbf{Equation 2}$$



28

4,10-diaza 18-crown-6[51]

Preliminary experiments on another diaza crown ether, i.e, **28**, gave "flat" results wherein virtually no selectivity for any of the alkali metal ions was observed. Further results in the literature were found[43,56,57] where this phenomena had been encountered when dealing with aza crown ethers. It was thought that protonation of amine nitrogen atoms occurs at the pH employed during the extraction experiments, with the result that protonated host compound simply extracts picrate as the counter-ion (i.e., in the absence of the corresponding alkali metal cation), as illustrated by equation 3.

$$H_2O_{(l)} + M^+_{(aq)} + Pic^-_{(aq)} + C_{(org)} \rightleftharpoons [C\ H^+ Pic^-]_{(org)} + M^+_{(aq)} + OH^-_{(aq)} \qquad \textbf{Equation 3}$$

In order to resolve this question, extraction experiments were carried out by adjusting the pH of the aqueous phase to pH 11-12 via addition of excess alkali metal hydroxide (see the Experimental Section).[56] In Table 4, the "flat" extraction results are compared with the corresponding results obtained under basic conditions (pH 11-12).

Table 4. Alkali metal picrate extraction results for compound **28** (% alkali metal picrate extracted).

	Li^+	**Na^+**	**K^+**	**Rb^+**	**Cs^+**
No pH control	20.2 ± 2.2	24.3 ± 1.8	21.7 ± 0.7	20.9 ± 0.9	24.3 ± 1.1
pH 11-12	2.9 ± 1.0	3.8 ± 1.5	11.3 ± 1.2	5.6 ± 1.6	3.7 ± 0.4

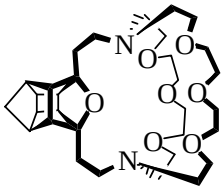
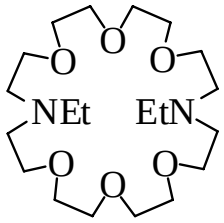
Here, it can be seen that under basic conditions the extraction avidity toward all alkali metal cations is reduced significantly. However, some selectivity is observed for K^+ under these conditions. These results suggest that the pH is a factor that must be considered when performing alkali metal picrate extraction experiments that employ basic *N*-containing host compounds.

Gokel[11] commented that there is a significant difference in ionic strength between an aqueous picrate solution and that of the corresponding alkali metal picrate solution that has been prepared by using an excess of the metal hydroxide. For the purpose of these alkali metal picrate extraction experiments that employ cryptand **15** and the corresponding model compound, **27**, comparison of the results should not be a problem, since both compounds were tested under exactly the same conditions. However, when

comparing the results from this study with any others that have been reported previously or that may be obtained in the future, inconsistencies may be present due to variables in the extraction technique employed (e.g., ionic strength, solution temperature, vigor of mixing, etc).[11]

The results of alkali metal picrate extraction experiments carried out at pH 11-12 and performed by using **15** and **27** as the host molecules are shown in Table 5.

Table 5. Alkali metal picrate extraction results for compounds **15** and **27** (% alkali metal picrate extracted).

	Li^+	**Na^+**	**K^+**	**Rb^+**	**Cs^+**
 **15**	5.8 ± 0.8	13.0 ± 0.6	34.2 ± 0.8	51.7 ± 0.6	53.3 ± 1.3
 **27**	9.4 ± 0.4	11.1 ± 0.5	17.9 ± 1.4	14.2 ± 0.6	15.4 ± 0.9

Therein, it can be seen that cryptand **15** displays generally higher avidity as an alkali metal picrate extractant than does the corresponding model compound, **27**, particularly toward K^+, Rb^+, and Cs^+. The cryptand shows enhanced avidity toward Rb^+ and Cs^+ *vis-à-vis* the other alkali metal cations, although there is little differentiation between these

two cations. This observation stands in agreement with results observed previously in the literature.[16] The flexibility of larger cryptands results in less size-complementarity between cavity and guest with concomitant loss of selectivity toward complex formation with the larger alkali metal cations.

Conclusions

Cage-[3.3.1] cryptand, **15**, was prepared and was fully characterized in an effort to extend the series from the previously reported cage-[2.2.1] cryptand, **9**.[45] Compound **9** was found to display very high avidity toward extraction of Na^+ via alkali metal picrate extraction experiments.

Alkali metal picrate extraction experiments were performed by using cryptand **15** and the corresponding model compound, **27**, as hosts. The extraction experiments were performed at pH 11-12 to avoid potential problems that might arise due to the presence of basic amine functionalities in these host molecules. Cryptand **15** displayed enhanced extraction *vis-à-vis* that of the model compound for all cations tested, except Li^+. In addition, cryptand **15** showed selectivity toward extraction of Rb^+ and Cs^+, albeit with little differentiation between the two ions. This result probably reflects the high degree of conformational mobility attendant with such a large cryptand structure.

Experimental Section

Melting points are uncorrected. Absorption intensities of alkali metal picrate solutions were measured at $\lambda = 374$ nm by using a Hewlett-Packard Model 24524 Diode Array UV-visible spectrophotometer. A pH meter equipped with a glass electrode was standardized at pH 7 and 10 using standard solutions. High-resolution mass spectral data reported herein were obtained by Professor Jennifer S. Brodbelt at the Mass Spectrometry Facility at the Department of Chemistry and Biochemistry, University of Texas at Austin by using a ZAB-E double sector high resolution mass spectrometer (Micromass, Manchester, England) that was operated in chemical ionization mode. Elemental microanalyses were performed by personnel at M-H-W Laboratories, Pheonix, AZ.

***exo*-8-*exo*-11-Diallylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-*endo*-8-*endo*-11-diol (18).**[41b] To a slurry of activated Mg (15 g, 0.617 mol) in dry Et_2O (125 mL) under argon was added dropwise with stirring a solution of freshly distilled allyl bromide (25 mL, 35.8 g, 0.296 mol) in dry Et_2O (175 mL) at such a rate (*ca*. 4 h) that the internal temperature did not rise above 5 C. After the addition of allyl bromide had been completed, the reaction mixture was allowed to stir at ambient temperature during 17 h and then was refluxed for 2 h. The resulting Grignard solution was transferred under argon to another flask. Ether was removed *in vacuo*, and dry THF (200 mL) was added. The resulting solution was cooled to 0 C (via application of an external ice-water bath). To this cooled solution was added slowly with stirring a solution of **17**[49b] (8.5 g, 49 mmol) in

dry THF (50 mL). After the addition had been completed, the ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature while stirring under argon during 20 h. The reaction mixture was cooled once again to 0 C (ice-water bath), and the reaction was quenched via careful addition of saturated aqueous NH_4Cl (50 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 70 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was recrystallized from hexane, thereby affording **18** (6.6 g, 52%) as a colorless microcrystalline solid: mp 82-83 C; IR (KBr) 3169 (s), 2976 (s), 1639 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (*A*B, J_{AB} =10.6 Hz, 1 H), 1.46 (A*B*, J_{AB} =10.6 Hz, 1 H), 1.89-2.19 (m, 6 H), 2.22-2.52 (m, 6 H), 4.89-5.08 (m, 4 H), 5.73-6.00 (m, 2 H), 6.91 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.6 (t), 39.7 (d), 42.6 (d), 43.8 (d), 43.8 (t), 48.8 (d), 77.0 (s), 117.0 (t), 133.6 (d); Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.14; H, 8.42.

3,5-Diallyl-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (19).[41b,42] To a solution of **18** (6 g, 232 mmol) in benzene (120 mL) was added TsOH (350 mg, 1.8 mmol, catalytic amount) and the resulting mixture was refluxed in a Dean-Stark apparatus during 36 h. Additional TsOH (350 mg) was added at 12 h intervals. The reaction mixture was allowed to cool gradually to ambient temperature and then was washed sequentially with 10% aqueous $NaHCO_3$ (50 mL), water (50 mL) and brine (50 mL). The layers were separated; the organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel

by eluting with 5% EtOAc-hexane. Pure **19** (3.4 g, 62%) was thereby obtained as a colorless oil; IR (film) 3075 (m), 2965 (s), 1640 (m), 997 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (*A*B, J_{AB} =10.2 Hz, 1 H), 1.82 (A*B*, J_{AB} = 10.2 Hz, 1 H), 2.35 (br s, 2 H), 2.45-2.65 (m, 10 H), 4.96-5.15 (m, 4 H), 5.67-5.90 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.3 (t), 41.5 (d), 43.1 (t), 44.3 (d), 47.6 (d), 58.4 (d), 94.8 (s), 116.5 (t), 134.2 (d); Exact mass (CI HRMS) Calcd for $C_{17}H_{20}O$: $[M_r + H]^+$ *m/z* 241.1592. Found: $[M_r + H]^+$ *m/z* 241.1601.

3,5-[2 ,2 -Bis(hydroxyethyl)]-4-oxahexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]-dodecane (20).[40] A two-neck round bottom flask equipped with a bubbler and a magnetic stirrer was charged with a solution of **19** (5.95 g, 24.8 mmol) in freshly dried MeOH (200 mL), and the reaction vessel was cooled to -78°C via immersion in an external dry ice-acetone cold bath. Ozone was bubbled through this solution until a blue color persisted (*ca*. 1 h), at which time the ozone source was disconnected from the reaction flask. Argon was bubbled through the cold reaction mixture to purge excess ozone, and this was followed by dropwise addition of Me_2S (5 mL, 68 mmol) with stirring to the cold (-78°C) reaction mixture. After the addition of Me_2S had been completed, the external cold bath was removed, and the resulting mixture was allowed to warm gradually to ambient temperature while stirring during 2 h. The reaction mixture was cooled to 0°C via application of an external ice-water bath, and $NaBH_4$ (2.0g, 53 mmol, excess) was added portionwise to the reaction mixture at such a rate that the internal temperature did not exceed 5 CAfter all the $NaBH_4$ had been added, the external ice-water bath was

removed, and the reaction mixture was allowed to warm gradually to ambient temperature while stirring during 4 h. Concentrated aqueous HCl was added dropwise to adjust the pH to *ca*. 5; then solid $NaHCO_3$ (2 g, 24 mmol) and solid NaCl (5 g, 86 mmol) were added sequentially to the reaction mixture. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was extracted sequentially with $CHCl_3$ (2 × 75 mL) and EtOAc (2 × 75 mL). The combined organic layers were washed sequentially with water (75 mL), and brine (75 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 30% EtOAc-hexane. Pure **20** (5.6 g, 91%) was thereby obtained as a colorless microcrystalline solid: mp 153.0-153.5 °C; IR (nujol) 3320 (m), 2980 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52 (*A*B *J* =10.5 Hz, 1 H), 1.88 (A*B*, *J* =10.5 Hz, 1 H), 2.01 (t, *J* =6.2 Hz, 4 H), 2.32-2.47 (m, 4 H), 2.52-2.68 (m, 6 H), 3.75 (t, *J* =6.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 34.3 (t), 41.4 (d), 43.5 (t), 44.1 (d), 47.7 (d), 58.2 (d), 60.1 (t), 96.4 (s); Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.65; H, 8.06.

3,5-Bis[2 ,2 -(*p*-toluenesulfonyloxy)ethyl]-4-oxahexacyclo-[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (21).[42,45] To a solution of **20** (8.81 g, 35.5 mmol) and Et_3N (29.7 mL, 213.2 mmol) in dry CH_2Cl_2 (120 mL) at 0 °C (ice-water bath) was added TsCl (16.93 g, 88.8 mmol) portionwise during 30 minutes. After the addition of TsCl had been completed, the reaction mixture was allowed to warm gradually to ambient temperature while stirring during 24 h. The reaction mixture was diluted with CH_2Cl_2 (120 mL), and then was extracted sequentially with water (2 × 75 mL) and brine (75 mL).

The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 50 % EtOAc-hexane. Pure **21** (15.0 g, 76 %) was thereby obtained as a colorless, low melting solid: ^{1}H NMR ($CDCl_3$) δ 1.45 (*A*B J_{AB} =10.5 Hz, 1 H), 1.79 (A*B*, J_{AB} =10.5 Hz, 1 H), 2.05 (t, J =7.0 Hz, 4 H), 2.27-2.63 (m, 14 H), 4.06 (t, J =7.0 Hz, 4 H), 7.31 (*A*B, J_{AB} =8.2 Hz, 4 H), 7.73 (A*B*, J_{AB} =8.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 31.7 (t), 41.5 (d), 43.4 (t), 44.1 (d), 48.2 (d), 58.7 (d), 67.5 (t), 93.5 (s), 127.8 (d), 129.8 (d), 133.1(s), 144.7 (s).

1,11-Dichloro-3,6,9-trioxaundecane (22).[50] To a solution of tetraethylene glycol (35.6 g, 0.183 mol) in dry 1,4-dioxane (40 mL) was added dropwise with stirring a mixture of $SOCl_2$ (52.8 g, 32.4 mL, 0.444 mol) and dry pyridine (2 mL). After the addition of $SOCl_2$ had been completed, the mixture was refluxed during 6 h and then was allowed to cool gradually to ambient temperature. The reaction mixture was concentrated *in vacuo* to remove solvent and excess $SOCl_2$. The residue was filtered through a pad of silica gel. The filtrate was dissolved in $CHCl_3$ (100 mL), and the resulting solution was washed with water (2 × 100 mL). The organic layer was dried ($MgSO_4$) and filtered, the filtrate was concentrated *in vacuo* to afford **22** (37.2 g, 88%) as a yellow oil: IR (film) 2935 (s), 2840 (vs), 2715 (w), 1490 (m), 1430 (m), 1340 (m), 1285 (s), 1240 (m), 1185 (m), 1100 (vs), 1035 (s), 820 (w), 735 (m), 655 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.50-3.61 (m, 12 H), 3.62-3.72 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 42.6 (t), 70.4 (t, 2 C), 71.1 (t).

1,11-Bis(benzylamino)-3,6,9-trioxaundecane (23).[51] A mixture of **22** (20 g, 0.0865 mol) and benzylamine (139 g, 156 mL, 1.298 mol) was heated at 120 ¡C during 3 days. The reaction mixture was allowed to cool to ambient temperature. Solid NaOH (6.617 g, 0.165 mol) was added, and the resulting mixture was heated to 120 ¡C during 1 h. Excess benzylamine was removed via vacuum distillation. The residue was dissolved in $CHCl_3$ (200 mL), and washed with water (2 × 200mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*, thereby affording **23** (29.4 g, 91%) as an orange oil: IR (film) 3028 (w), 2865 (m), 1122 (s), 737 (m), 698 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (s, 2 H), 2.76 (t, *J* =5.3 Hz, 4 H), 3.50-3.65 (m, 12 H), 3.78 (s, 4 H), 7.15-7.38 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 48.6 (t), 53.7 (t), 70.2 (t), 70.4 (t), 70.5 (t), 126.7 (d), 128.0 (d), 128.2 (d), 140.2 (s).

10,22-Bis(phenylmethyl)-10,22-diaza-1,4,7,13,16,19-hexaoxa-cyclotetracosane (24).[52] A mixture of **22** (4.29 g, 18 mmol), **23** (5.60 g, 15 mmol), KI (15.0 g, 90 mmol), Cs_2CO_3 (7.39 g, 23 mmol) and K_2CO_3 (9.33 g, 67 mmol) was refluxed in dry CH_3CN (400mL) during 5 days. The mixture was allowed to cool to ambient temperature and then was filtered. The filtrate was concentrated *in vacuo*, and the residue thereby obtained was purified via column chromatography on silica gel (5% MeOH-EtOAc) to give **24** (2.51 g, 31%) as an orange oil: IR (film) 3040 (w), 3010 (w), 2840 (s), 1480 (w), 1435 (m), 1335 (m), 1285 (m), 1240 (m), 1105 (m), 735 (s), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.78 (t, *J* =5.8 Hz, 8 H), 3.52-3.72 (m, 28 H), 7.15-7.38 (m, 10 H); ^{13}C

NMR ($CDCl_3$) δ 53.7 (t), 59.8 (t), 69.9 (t), 70.5 (t), 70.7 (t), 126.7 (d), 128.0 (d), 128.7 (d), 139.6 (s).

10,22-Diaza-1,4,7,13,16,19-hexaoxacyclotetracosane (25).[53,54] To a solution of **24** (2.50 g, 4.69 mmol) in MeOH (100 mL) was added 10% palladized charcoal (300 mg). The resulting mixture was subjected to hydrogenolysis on a Parr hydrogenation apparatus by agitation with excess H_2 (g) at 55 psig at ambient temperature during 3 days. The reaction mixture was filtered through a Celite pad to remove spent catalyst. The filtrate was concentrated *in vacuo* to yield **25** (1.2 g, 73%) as a yellow oil: IR (film) 3370 (w), 2935 (s), 1440 (s), 2390 (m), 1465 (m), 1445 (m), 1375 (w), 1350 (m), 1330 (m), 1290 (m), 1120 (s), 1065 (s), 1020 (m), 925 (s), 900 (m), 820 (m), 730 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (t, J =5.0 Hz, 8 H), 3.52-3.65 (m, 24 H), 3.78 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 48.6 (t), 69.7 (t), 70.3 (t), 70.5 (t).

Cage-[3.3.1] cryptand (15). A mixture of **25** (359 mg, 1.03 mmol), **21**[45] (571 mg, 1.03 mmol) and Cs_2CO_3 (1.46 g, 4.47 mmol) in dry CH_3CN (60 mL) was refluxed during 5 days and then was allowed to cool gradually to ambient temperature. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by using a gradient elution scheme (80-100% MeOH-EtOAc). The eluate thereby obtained consisted of both complexed and non-complexed ligand. This mixture was dissolved in $CHCl_3$ (50 mL) and was shaken mechanically with water (50 mL) during 4 days. The aqueous layer was withdrawn and was replaced with fresh water every 24 h. The $CHCl_3$ layer was dried ($MgSO_4$) and

filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on basic alumina by eluting with EtOAc. Pure **15** (260 mg, 43%) was thereby obtained as a yellow oil: IR (film) 2920 (s), 2830 (s), 1675 (w), 1435 (m), 1335 (m), 1280 (m), 1100 (s), 970 (m), 920 (m), 860 (w), 750 (m), 690 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (*A*B, J_{AB} =10.3 Hz,1 H), 1.75-2.00 (m, 5 H), 2.26-2.88 (m, 20 H), 3.45-3.70 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 29.6 (t, 2 C), 41.3 (d, 2 C), 43.5 (t), 43.8 (d, 2 C), 47.8 (d, 2 C), 50.2 (t, 2 C), 54.0 (t, 4 C), 58.5 (d, 2 C), 69.6 (t, 2 C), 69.9 (t, 2 C), 70.4 (t, 2 C), 70.5 (t, 2 C), 70.7 (t, 2 C), 70.8 (t, 2 C), 94.9 (s, 2 C). A gated-decoupled ^{13}C NMR experiment was performed to permit integration of the ^{13}C NMR spectrum. Exact mass (CI HRMS) Calcd for $C_{31}H_{50}N_2O_7$: $[M_r + H]^+$ *m/z* 563.369628, Found: $[M_r + H]^+$ *m/z* 563.369421.

10,22-Diacetyl-10,22-diaza-1,4,7,13,16,19-Hexaoxacyclotetracosane (26).[18] To a solution of **25** (820 mg, 2.34 mmol), DMAP (57 mg, 0.468 mmol), Et_3N (824 mg, 1.1 mL) in dry CH_2Cl_2 (40 mL) was added freshly distilled Ac_2O (529 mg, 0.49 mL, 5.19 mmol). The reaction mixture was refluxed during 2 days and then was allowed to cool to ambient temperature. The reaction mixture was washed with water (3 × 50 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel (5% MeOH-$CHCl_3$) to give **26** (280mg, 27%) as a colorless, waxy solid. Compound **26** was recrystallized from CH_2Cl_2-hexane to yield colorless crystals: m.p. 85.5-86.5 °C: IR (KBr) 2880 (m), 2865 (m), 1638 (s), 1100 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (s, 6 H), 3.48-3.65 (m, 32 H); ^{13}C

NMR ($CDCl_3$) δ 21.6 (q, 2 C), 46.6 (t), 46.8 (t), 49.9 (t, 2 C), 69.4 (t), 69.6 (t), 69.7 (t), 70.0 (t), 70.3 (t), 70.4 (t), 70.5 (t), 70.56 (t, 2 C), 70.62 (t), 70.8 (t), 71.0 (t), 171.0 (s, 2 C); Anal. Calcd for $C_{20}H_{38}N_2O_8$: C, 55.26; H, 8.82. Found: C, 55.35; H, 8.76.

10,22-Diaza-10,22-diethyl-1,4,7,13,16,19-Hexaoxacyclotetracosane (27). A solution of **26** (250 mg, 0.575 mmol) in dry THF (20 mL) was added to a cooled (ice-water bath) suspension of $LiAlH_4$ (218 mg, 5.75 mmol) in dry THF (50mL). After the addition of **26** had been completed, the reaction mixture was refluxed during 4 days. The reaction was quenched via careful, dropwise addition of saturated aqueous Na_2SO_4 (3 mL, excess) with stirring to the reaction mixture. The resulting mixture was filtered through a Na_2SO_4 pad, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on basic alumina (1% MeOH-CH_2Cl_2), thereby affording **27** (108 mg, 46%) as a yellow oil: IR (film) 2960-2800 (br, s), 1452 (m), 1348 (m), 1292 (m), 1254 (m), 1140 (s), 1094 (s), 833 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (t, J =7.1 Hz, 6 H), 2.58 (q, J =7.1 Hz, 4 H), 2.72 (t, J =5.9 Hz, 8 H), 3.50-3.65 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 11.8 (q), 49.3 (t), 53.3 (t), 69.7 (t), 70.5 (t), 70.7 (t); Exact mass (CI HRMS) Calcd for $C_{20}H_{43}N_2O_6$: $[M_r + H]^+$ *m/z* 407.312113, Found: $[M_r + H]^+$ *m/z* 407.313011.

Alkali metal picrate extraction experiments. The general procedures employed herein are similar to those reported previously.[55,56] Aqueous solutions of the alkali metal hydroxides (125 mM) were prepared. In experiments where no pH adjustment was required, a 5mM aqueous solution of the alkali metal picrate was prepared as follows; into a 25 mL volumetric flask was placed picric acid (28.6 mg, 0.125

mmol) and water (5 mL), and an aliquot (1 mL) of the 125 mM aqueous metal hydroxide solution was added. The resulting mixture was shaken to effect complete dissolution, at which time the solution was diluted by the addition of water to volume (25 mL). To adjust the pH to 11-12, the solution was prepared in a similar manner except that three 1 mL aliquots of the 125 mM aqueous metal hydroxide solution were added. $CHCl_3$ was washed with water to remove EtOH, and then was used to prepare 5 mM solutions of each of the compounds to be tested.

Aliquots (0.5 mL) of the $CHCl_3$ solutions that contained host compound and the aqueous solution that contained the metal picrate were introduced into a screw-topped vial and then were shaken mechanically at ambient temperature during 30 minutes. The resulting mixtures were allowed to stand for at least 2 hours at ambient temperature in order to effect complete phase separation. A 50 μL aliquot was transferred from the aqueous phase of each vial into a 25 mL volumetric flask and was diluted to volume by addition of CH_3CN. The UV/Vis absorption of the solution was measured at λ = 374 nm. A control experiment (blank) was performed for each alkali metal picrate solution, wherein no host was present in the $CHCl_3$ layer. For each host and alkali metal picrate combination, three separate experiments were performed in three separate vials. Two separate CH_3CN solutions were prepared for each vial, and their absorbances were measured at λ = 374 nm. The percentage of alkali metal picrate that had been extracted into the organic phase by a particular host was calculated by using equation 4.

$$\% \text{ extracted} = \frac{(\text{absorbance of blank}) - (\text{absorbance of sample})}{(\text{absorbance of blank})} \times 100 \qquad \textbf{Equation 4}$$

A complete listing of extraction data thereby obtained appears in Appendix A.

CHAPTER THREE

A COMPUTATIONAL STUDY OF SOME CAGE-FUNCTIONALIZED CRYPTANDS AND THEIR ALKALI METAL COMPLEXES

Roughly three decades years ago, when exploration of supramolecular chemistry was in its infancy, Pedersen, Lehn, and Cram, among others, performed molecular modeling studies by using Corey-Pauling-Koltun (CPK) models, in order to design host molecules that might be capable of binding to specific guests. Since then, advances in technology have increased the numbers and kinds of modeling capabilities that are routinely available. To date, crown ethers have been studied by a variety of molecular modeling techniques.[58] In particular, 18-crown-6 has been subjected to various types of computational modeling techniques including; e.g., molecular mechanics,[58,59] Monte-Carlo calculations,[58,60] conformational searches,[58,61] molecular dynamic simulations,[58,62,63] and extended basis set *ab initio* calculations.[64-67]. These methods have been used to model complexation of alkali metal cations in the gas phase,[64-67] in water[58,68] and in non-aqueous solvents,[58,69] and also to model complexation of neutral species,[58,70]

Computational studies of cryptands and cryptates have been less extensive. Dearden and co-workers performed molecular mechanics modeling with the AMBER force field.[71] The geometries obtained for alkali metal cation complexes of [2.1.1], [2.2.1] and [2.2.2] cryptand were compared with experimental results obtained under solvent

free, gas phase conditions using Fourier transform with ion cyclotron resonance mass spectrometry, and were found to be generally consistent.

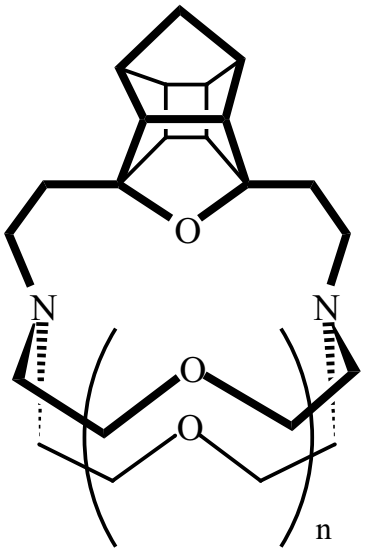
Wipff and co-workers have performed a more intensive study of [2.2.2] cryptand and its properties.[72-75] By using High Temperature Annealed Molecular Dynamics Simulations , searches were performed for; (i) the lowest energy structures, (ii) structures suitable for inclusion of a particular host, and (iii) structures that correspond to the experimentally determined solid state structures.[72] They concluded that the lowest energy conformation of the free host will not necessarily be suitable for complexation with a guest. Thus, inclusion of the guest in the simulation is necessary to replicate the conformations found experimentally for several complexes.[72]

In other studies that employed using molecular dynamics calculations which were performed by using the AMBER program, the effect of solvation was investigated. It has been found experimentally that ligand-solvent interactions have an important effect upon the stabilities of ligand-metal cation complexes, despite the fact that they have relatively weak interactions in comparison to solvent-metal cation interactions.[76,77] The results of these computational studies indicated that conformations of both the free and complexed ligand were altered by the addition of water solvent.[73]

Free energy perturbation calculations were performed to predict relative free energies of complexation of Na^+, K^+ and Rb^+ by [2.2.2] cryptand in water and MeOH.[74] The procedure employed an initial structure from a known X-ray crystal structure of the K^+-[2.2.2] cryptand complex. The computational process then involved mutation of K^+ into Na^+ and Rb^+ respectively, by a slow growth technique. The relative free energies for the complexes were then compared. In the gas phase, the order of binding affinities

was calculated to be $Na^+ > K^+ > Rb^+$, a result which is consistent with previous molecular mechanics optimizations.[75] When solvent molecules were added to the same calculations, the selectivity was altered, and the highest binding affinity was found for K^+. However, when a more compact K^+-[2.2.2] cryptand complex structure was used as the starting structure for the exact same computations, binding to Na^+ was preferred in both the gas phase and solution. It was concluded that the ability of these types of calculations to predict relative binding affinities of cryptand receptors is questionable when experimentally established structures are not available.[74]

The aim of the present study is to use *ab initio* calculations to correlate the relative binding energy trends of alkali metal complexes of cage-functionalized cryptands with the corresponding trends observed experimentally via alkali metal picrate extraction experiments. The series of cage-functionalized cryptands which were used for this study is shown in Figure 11.



29 (n=1) cage-[1.1.1] cryptand
9 (n=2) cage-[2.2.1] cryptand
15 (n=3) cage-[3.3.1] cryptand

Figure 11. The cryptand series investigated in this computational study.

Experimental Section

Initial structures were obtained via Monte Carlo conformer searches by using the MMFF94 force field with SPARTAN.[78] Since SPARTAN cannot incorporate electrostatic interactions, it was necessary to specify which of the available donor atoms were bonded to the cation. Both covalent and hydrogen bond types were used, and these bonds were altered systematically in order to locate the lowest energy conformation. The conformations obtained were then submitted as input coordinates for *ab initio* geometry optimizations, which were performed at the Hartree-Fock (HF) level of theory with the 3-21G basis set as executed in Gaussian 98.[79] Geometry optimizations also were performed in this manner for the "free" cryptands and for the individual alkali metal cations. Subsequent single-point energy calculations were carried out by using 6-31G, and 6-311G basis sets for some of the structures thereby obtained in order to assess the appropriate basis set limit for these systems at the HF level of theory. Cartesian coordinates for all of the uncomplexed and complexed cryptand structures obtained are reported in Appendix B. Molecular mechanics calculations were performed on an Indigo 2 SGI work station. *Ab initio* calculations were performed on the SGI/Cray Origin 2000 at Boston University, Center for Computational Sciences (CCS) through the National Computational Science Alliance (NCSA).

Results and Discussion

Binding Energies

$$\Delta E = E_{CM} - E_C - E_M \qquad \text{Equation 5}$$

The binding energy (ΔE) for each complex considered was calculated by using Equation 5. The total energies of the uncomplexed "free" cryptand (E_C) and the naked alkali metal cation (E_M) were subtracted from the total energy for the complex (E_{CM}). The difference was considered to reflect the binding energy, i.e. the additional stability gained by formation of the complex. The results obtained from the geometry optimization (HF/ 3-21G) and subsequent single point energy calculations (HF/ 6-31G and HF/ 6-311G) are listed in the Tables 6-8 below.

Table 6. Binding energies (kcal/ mol) calculated for alkali metal complexes of cage-[1.1.1] cryptand (**29**).

M^+	Level of Theory/ Basis Set	
	HF/ 3-21G	**HF/ 6-31G**
Li^+	-167.5	-143.2
Na^+	-121.0	-90.0
K^+	-29.0	-17.4
Rb^+	-24.4	-20.9
Cs^+	-15.9	-16.2

Table 7. Binding energies (kcal/ mol) calculated for alkali metal complexes of cage-[2.2.1] cryptand (**9**).

M^+	Level of Theory/ Basis Set		
	HF/ 3-21G	**HF/ 6-31G**	**HF/ 6-311G**
Li^+	-165.6	-134.8	_
Na^+	-140.1	-109.9	-106.5
K^+	-101.0	-78.3	_
Rb^+	-75.6	-55.6	_
Cs^+	-45.8	-37.6	_

Table 8. Binding energies (kcal/ mol) calculated for alkali metal complexes of cage-[3.3.1] cryptand (**15**).

M^+	Level of Theory/ Basis Set	
	HF/ 3-21G	**HF/ 6-31G**
Li^+	-135.4	-97.3
Na^+	-125.2	-78.8
K^+	-95.0	-68.6
Rb^+	-74.4	-61.9
Cs^+	-60.2	-57.5

For all three examples studied, binding energy decreases with increasing cation size. This may be the expected trend for the cage-[1.1.1] cryptand (**29**); however, the results of alkali metal picrate extraction experiments are known for cage-[2.2.1] cryptand

(**9**)[45] (see Table 3) and for cage-[3.3.1] cryptand (**15**) (see Table 5) and do not correlate with this trend. Similar results also have been reported for gas phase *ab initio* calculations with 18-crown-6[67] and for molecular mechanics calculations with [2.2.2] cryptand.[75] These results appear to only reflect electrostatic considerations and not coordination abilities. Thus, smaller alkali metal cations possess greater charge densities and thereby exert stronger electrostatic fields with which they might interact with electron-donating groups in the various ligands.[67]

Comparison of the results obtained with 3-21G and 6-31G basis sets indicates that a significant decrease in the complexation energy values is attendant with the use of the larger basis set. However, comparison of the results obtained with 6-31G and 6-311G basis sets for Na^+-cage-[2.2.1] cryptand (**9***Na^+) showed a much smaller decrease in the energy value. These results indicate that for these systems, 3-21G basis sets is not descriptive enough to begin to reach the basis set limit at the HF level of theory. Additionally, it appears that the use of any basis sets larger than 6-31G does not have a significant effect upon the result, thereby indicating close proximity to the basis set limit at much smaller computational cost. It should be noted that single-point energies obtained with the 6-31G basis set did not change the trends observed for the binding energies, with the exception of Rb^+-cage-[1.1.1] cryptand (**29***Rb^+).

Structures

It is understood that with such complex structures, in particular the larger more flexible cryptands, the "minimum energy conformations" found by calculation may not be the global minimum but may in fact represent a conformation that reflects one of

many possible local energy minima. In order to assess the quality of the calculations, a comparison was made with the X-ray crystal structure which has been previously reported for Na^+-cage[2.2.1] cryptand (**9***Na^+).[45] (Cartesian coordinates are listed in Appendix D).

A single point energy calculation performed at the HF/ 6-31G level of theory and basis set which utilized the coordinates from the X-ray crystal structure as input gave a total energy 426.3 kcal/ mol higher (i.e. less favorable) than the computationally obtained conformation. Probable reasons for such a large, unfavorable difference include: (i) the presence of crystal packing forces in the solid state crystal structure and (ii) uncertainty (– 0.1A) in the exact position of the atoms in the X-ray crystal structure due to bond vibrations which can occur at ambient temperature. Geometry optimizations of both the X-ray crystal structure and the previously obtained computational structure were performed using HF/ 6-31G and B3LYP/ 6-31G. The results thereby obtained are shown in Table 9. The binding energy calculated using the X-ray crystal structure coordinates as input is approximately 6 kcal/ mol lower in energy than the binding energy calculated using the HF/ 3-21G coordinates as input at both HF and B3LYP levels of theory.

Table 9. A comparison of the binding energies (kcal/ mol) obtained using different input coordinates of Na^+-cage-[2.2.1] cryptand (**9***Na^+).

	HF/ 6-31G	**B3LYP/ 6-31G**
Crystal Input	-117.5	-119.0
HF/ 3-21G Input	-111.0	-112.9

Comparison of the two structures obtained from the HF/ 6-31G geometry optimizations is presented in Figure 12. With the exception of the cage moiety, the two structures appear to be mirror images. From this investigation, it was concluded that the conformations obtained for all the geometry optimizations probably reflect "local energy minima" and not the "global energy minimum". However, the example shown in Figure 12 indicates that the actual global minimum conformations have reasonably similar geometries to the conformations obtained computationally.

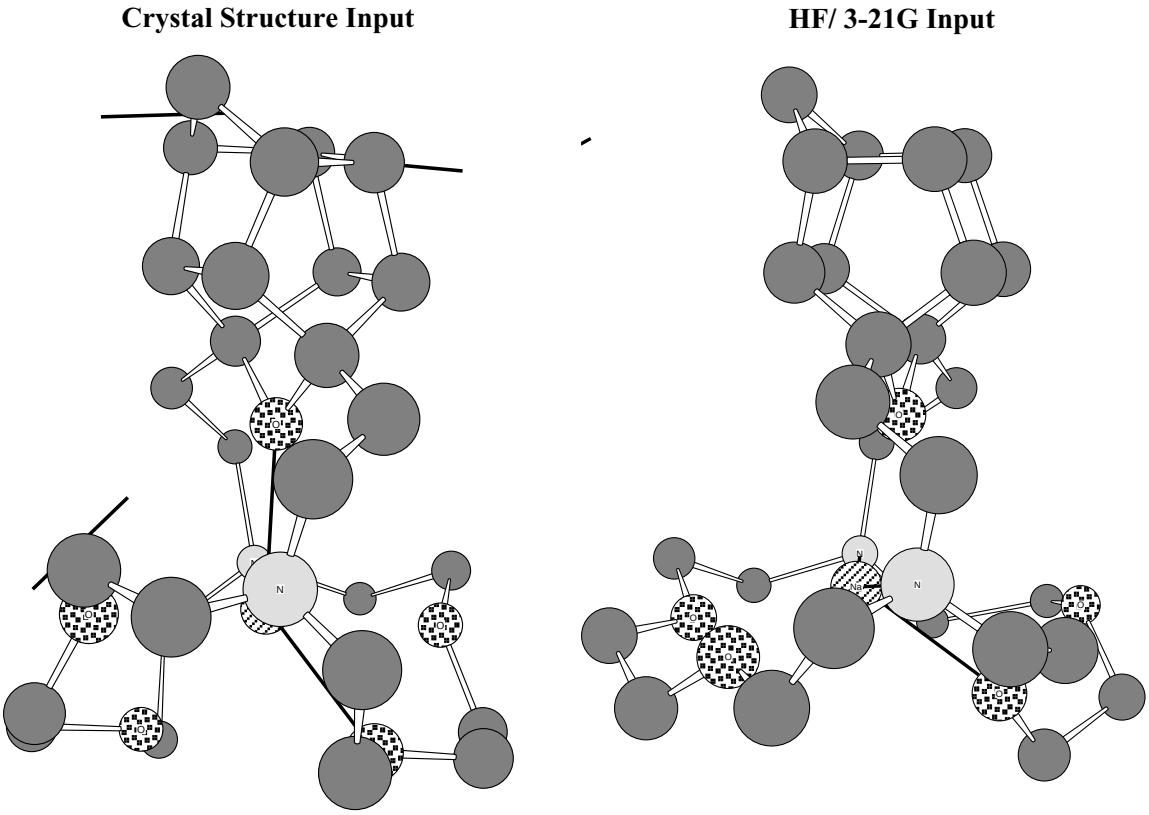


Figure 12. A comparison of the structures obtained from HF/ 6-31G geometry optimizations using the X-ray crystal structure coordinates and the previously obtained HF/ 3-21G geometry optimization coordinates of **9***Na^+ as input, respectively.

The conformations found by HF/ 3-21G geometry optimization for the alkali metal cryptates of cage-[1.1.1] cryptand (**29**) are shown in Figure 13a. As might be expected, Li^+ is bound inside the cavity in a fairly central position along the N-N axis. A similar structure is observed for Na^+; however K^+, Rb^+ and Cs^+ are excluded from the cavity, since they are too large.

The lowest energy conformations found for cryptates of cage-[2.2.1] cryptand (**9**) are shown in Figure 13b. Here, all of the cations except Cs^+ are located centrally within the cavity. In the inclusion complexes of both cage -[1.1.1] (**29**) and cage-[2.2.1] (**9**) cryptands, the cage ether oxygen is sufficiently proximal to the cation to be involved in complexation. This result is in agreement with the X-ray crystal structure of Na^+-cage[2.2.1] cryptand (**9***Na^+),[45] which indicates that this Na^+***O interaction is present.

The lowest energy structures found for cryptates of cage-[3.3.1] cryptand (**15**) are shown in Figure 13c. The alkali metal cation appears to be complexed in a very different manner by this cryptand than by the previous two cryptands. Here, the cation is positioned farther away from the cage moiety, below the N-N axis, with the cage ether oxygen too distant to be involved in complexation. Instead, the two "arms" of the cryptand wrap themselves around the cation in order to form the complex. Complexation in this manner might be dynamic and reversible (i.e. more like that of a crown ether than a traditional cryptand).

Conclusions

Binding energies for the cage-functionalized cryptands investigated indicate that the stability of the complexes depends primarily upon electrostatics, with the smallest,

most charge-dense cations having the largest binding energies. This result does not correlate with the trends observed from previously obtained picrate extraction experiments but is consistent with similar calculations reported in the literature.[67-75] In order to better rationalize these results, it will be necessary to modify the model. Possible ways to do this include; incorporation of the counter ion in the model and/ or inclusion of solvation.

The geometries obtained are probably the result of local energy minima and not the global minimum. However, the computationally and experimentally obtained structures of Na^+-cage[2.2.1] cryptand (**9***Na^+) are fairly similar. Inspection of the conformations thereby obtained for all the other alkali metal cryptates reveals that the cage-[3.3.1] cryptand (**15**) complexes cations in a manner different from that displayed by cage-[1.1.1] (**29**) and cage-[2.2.1] (**9)** cryptands. In the latter two cryptands, when the cation is of a suitable size to form inclusion complexes, the cation is located centrally in the cavity with all heteroatoms including the cage ether oxygen participating in complexation. In the cage-[3.3.1] cryptand (**15**), the cation is complexed below the N-N axis, with the two "arms" of the cryptand wrapping themselves around the cation. Here, the cage ether oxygen is not involved in complexation. This result may indicate that the inclusion complexes formed by cage -[3.3.1] cryptand (**15**) are not as stable as those formed by cage-[1.1.1] (**29**) and cage-[2.2.1] (**9**) cryptands.

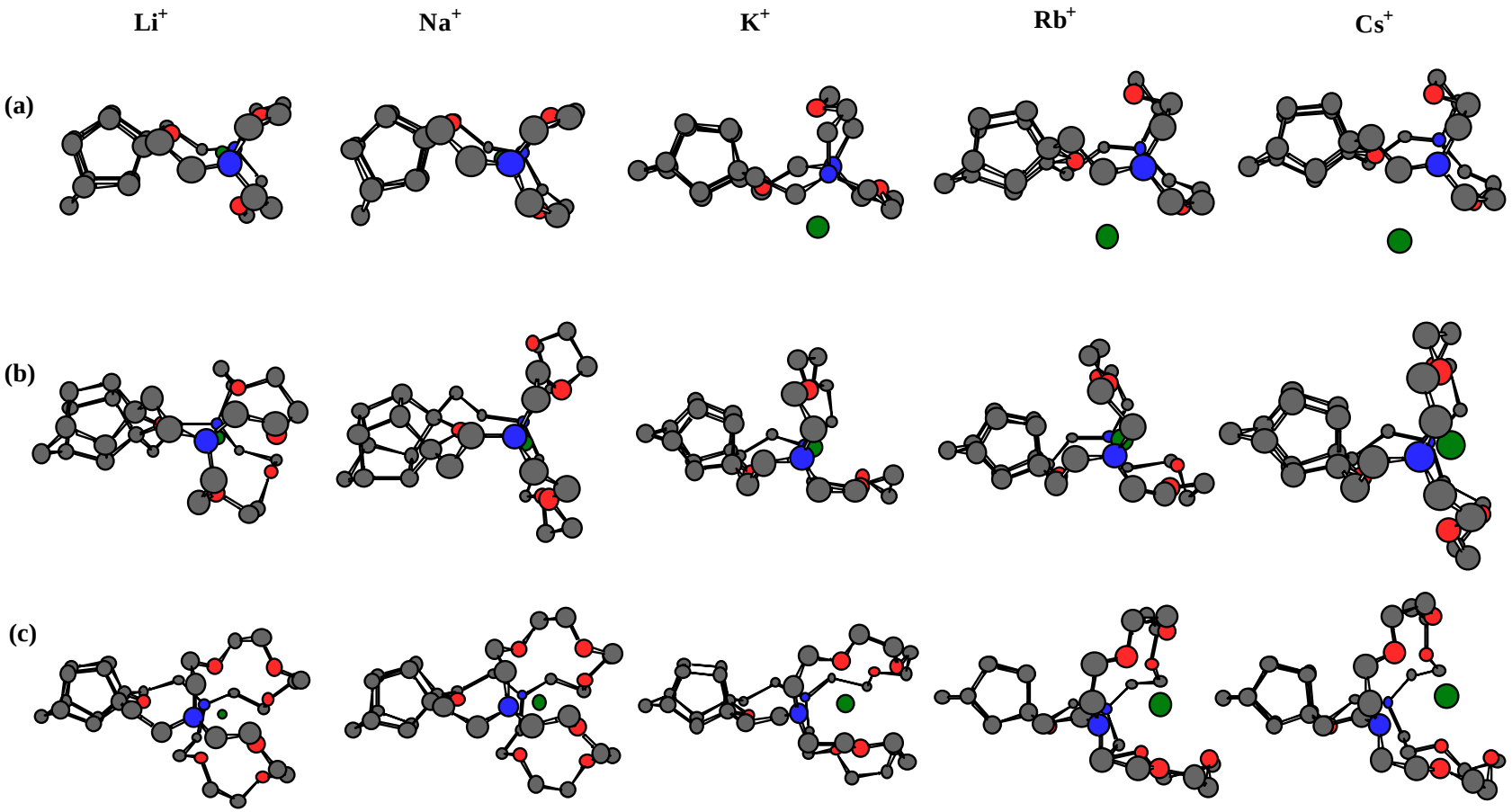
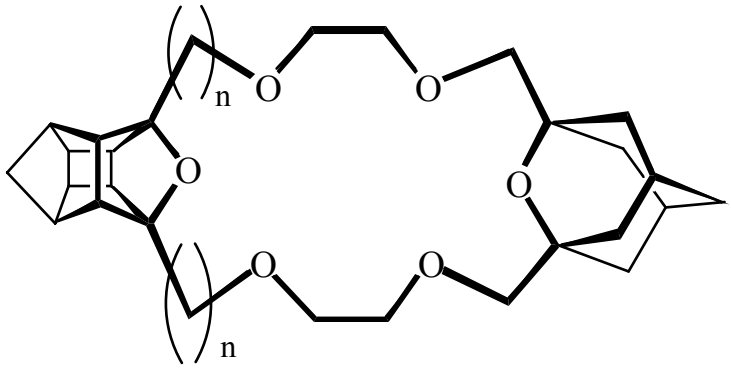


Figure 13. The structures of alkali metal cage-functionalized cryptates obtained from HF/ 3-21G geometry optimizations: (a) cage-[1.1.1] cryptates (**29**•M^+); (b) cage-[2.2.1] cryptates (**9**•M^+); (c) cage-[3.3.1] cryptates (**15**•M^+) (hydrogen atoms have been omitted for clarity, blue = nitrogen, red = oxygen, green = alkali metal cation).

CHAPTER FOUR

DETERMINATION OF THE INTERACTION ENERGY CONTRIBUTION OF PICRATE ANION TOWARD STABILIZATION OF A K^+ *BIS*-CAGE-ANNULATED 20-CROWN-6

As part of a continuing effort to develop host molecules that incorporate rigidifying, lipophilic, polycyclic moieties, crown ethers **30** and **31** were synthesized (Figure 14). They are closely related to a previously reported crown ether that contains two oxaadamantane units and which was found to have exceptional extraction avidity towards K^+ and Rb^+ via alkali metal picrate extraction experiments.[39]



30 n=1
31 n=2

Figure 14. *Bis*-cage-annulated crown ethers synthesized by Dr. Kata Mlinarić-Majerski, Rudjer Bŏsković Institute, Zagreb, Croatia.

Alkali metal picrate extraction experiments were performed by using crown ethers **30**, **31** and 18-crown-6, the latter of which serves as a corresponding model compound. The results thereby obtained are presented in Table 10. Ionophore **30**, displayed high

avidity towards all the alkali metal cations when compared with the model compound, particularly toward K^+. Ionophore **31** showed significantly reduced avidity toward all of the alkali metal cations *vis-à-vis* the corresponding model compound 18-crown-6. The results can be explained in terms of two key concepts in supramolecular chemistry:

(i) the size fit principle,[14] i.e., 18-crown-6 is known to have an ideal cavity size for K^+. With increase in cavity size to 20-crown-6, as in **31**, concomitant reduction in extraction is observed.

(ii) the principle of preorganization,[15] i.e., addition of two rigid polycyclic moieties to the 18-crown-6 structure confers both rigidity and preorganization to **31** with respect to 18-crown-6, with the result that enhanced extraction ability is observed.

Table 10. Alkali metal picrate extraction results for compounds **30**, **31** and 18-crown-6 (% alkali metal picrate extracted).

	Li^+	**Na^+**	**K^+**	**Rb^+**	**Cs^+**
30	4.8 ± 1.0	20.4 ± 1.0	71.2 ± 1.7	63.7 ± 0.3	52.5 ± 1.3
31	BLD*	BLD*	17.8 ± 1.0	11.4 ± 1.3	3.0 ± 0.5
18-crown-6	1.6 ± 1.2	5.1 ± 0.8	65.2 ± 0.5	49.0 ± 0.7	28.2 ± 0.9

*BLD = Below Limit of Detection

Single crystals of the K^+ picrate complexed **31** (mp 144-145 ^oC) were obtained by fractional recrystallization from CH_2Cl_2-hexane. The X-ray crystal structure[80] is shown in Figure 15. Potassium cation resides in the center of the crown ether cavity and appears to

be coordinated to all six ether oxygens. However, it is evident that the picrate anion also is intimately involved in stabilization of the host-guest complex.

A search of the literature confirmed that this was not an isolated case. Numerous examples of host-guest complexes of picrate salts, where picrate co-crystalizes are known.[81-87] Often, the picrate anion interactions were similar to those in the complex in Figure 15, i.e., the metal cation is coordinated to picrate anion through both the phenoxide and an *ortho* nitro oxygen.[81-83] However, in many cases the interactions of picrate ranged from no obvious interaction whatsoever[82,83] to interaction with only one functional group (phenoxide,[84] *o*-NO_2[85]) and, finally to more elaborate interactions in which one or more picrate anions coordinate with more than one cation:host complex into a layered "sandwich-type" structure.[82,86,87]

The present study is undertaken in an effort to estimate the interaction energy between picrate anion and the K^+-complexed *bis*-cage-annulated 20-crown-6 (**31**•K^+).

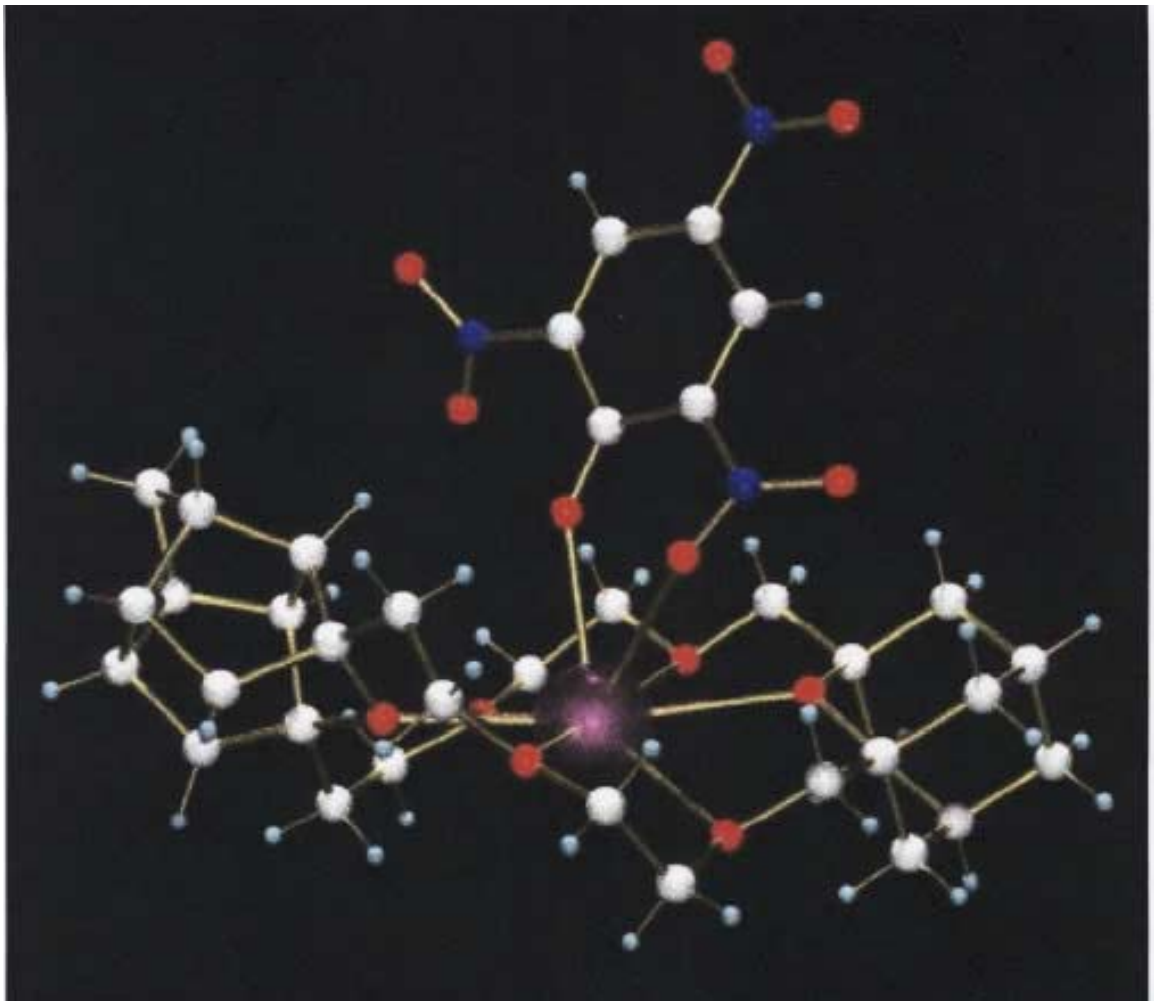


Figure 15. X-ray crystal structure drawing of K^+ picrate complexed **31**.[80]

Experimental Section

The X-ray crystal structure coordinates (see Appendix D) were used as input for B3LYP/ 6-31G geometry optimization. It is known from past experience that B3LYP is the lowest level of theory that should be used to obtain a geometry-optimized structure which compares well with the crystal structure. An overlay that permits comparison of the calculated structure (for cartesian coordinates see Appendix C) with the experimentally determined X-ray crystal structure is shown in Figure 16.

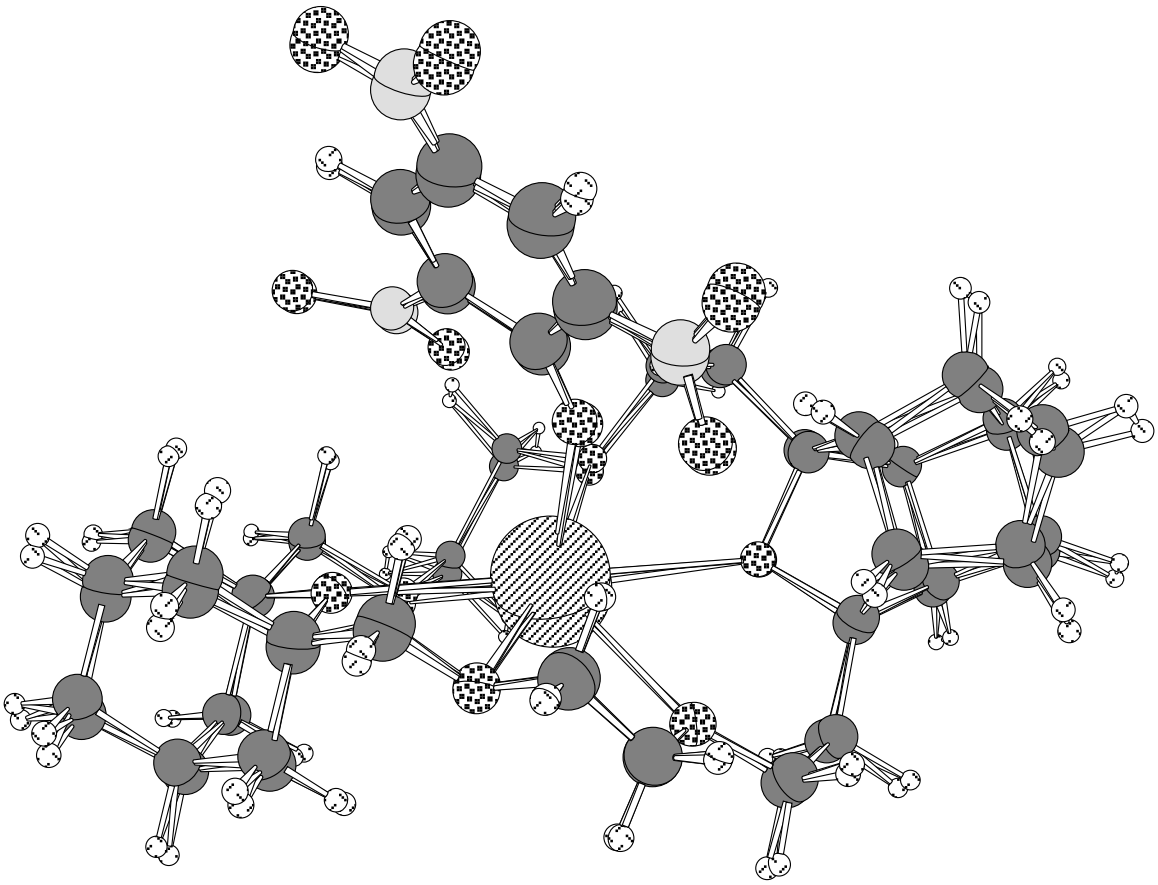


Figure 16. Overlay of the B3LYP/ 6-31G geometry optimization and the crystal structure (Hyperchem).[88]

An axis was defined between K^+ (atom 1) and the aromatic carbon of the picrate anion (atom 97) which is situated two atoms away from each of the picrate oxygen atoms that are involved in complexation with K^+ (see Figure 17). The picrate ion was systematically moved along the axis at 0.2 A increments between 4.25-5.85 A. At each incremental distance, B3LYP/ 6-31G partial geometry optimizations were performed. Geometry optimizations also were performed at distances of 4.0, 6.0, and 8.0 A. Counterpoise correction[89] was utilized to remove basis set superposition error (BSSE)[90] at each point optimized.

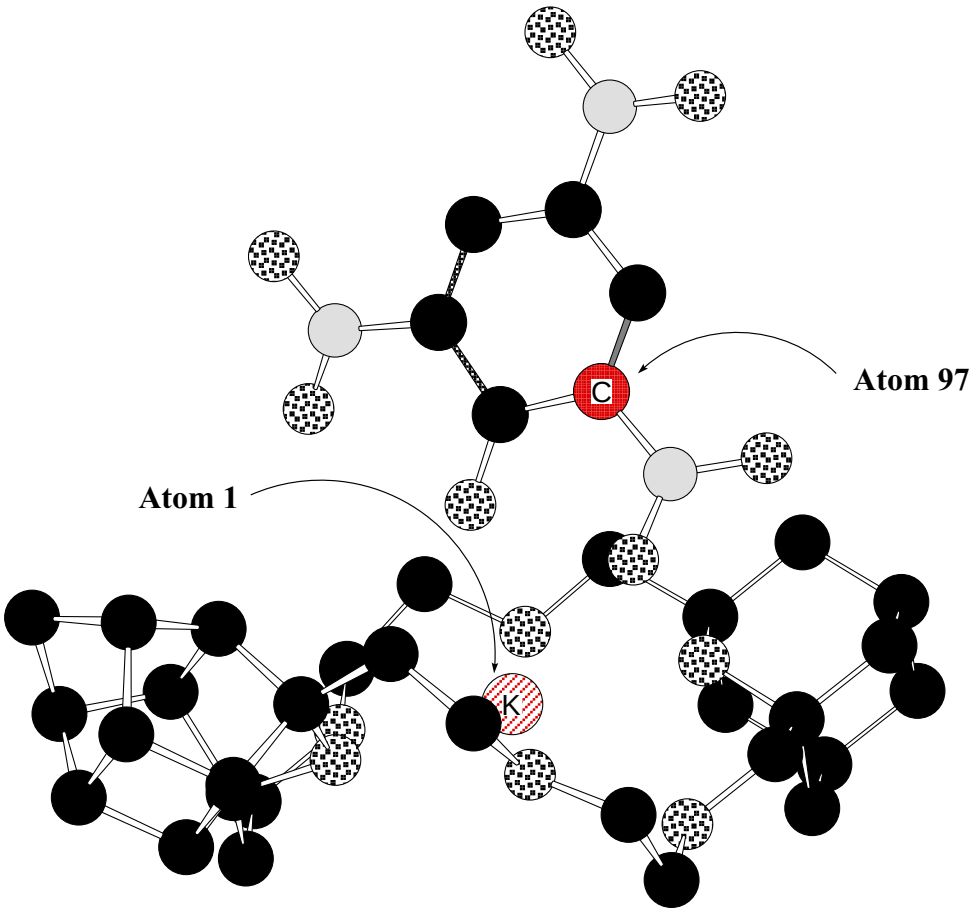


Figure 17. Definition of the axis (atom 1 — atom 97) along which the picrate anion was systematically moved at 0.2 A increments.

BSSE is a computational artifact present in calculations that involve non-covalent interactions. As the two interacting monomers approach each other they automatically take advantage of the basis set of the whole "dimer".[91] Consequently, the resulting intermolecular interactions are artificially overly attractive,[92] thereby narrowing the equilibrium distance between the two "monomers" with concomitant artificial lowering of the dimer energy and the interaction energy at the equilibrium geometry.[90]

Typically the interaction energy (ΔE),[90] is defined as:

$$\Delta E = E_{AB} - E_A - E_B \qquad \textbf{Equation 6}$$

where E_{AB} is the energy of the complex and E_A and E_B are the energies of the monomers A and B, respectively. However, BSSE is also present in the ΔE term when it is calculated in this way.

Counterpoise correction[89] has been proven as a method to overcome BSSE. In this technique the ΔE term described above (Equation 6) is labeled the "monomer centered basis set" interaction energy (ΔE_{MCBS}). A second calculation, the "dimer centered basis set" (DCBS) calculation is also performed. In this calculation the interaction energy is defined as:

$$\mathbf{\Delta E_{DCBS} = E_{AB} - E_A^{\{AB\}} - E_B^{\{AB\}}} \qquad \textbf{Equation 7}$$

where E_{AB} is the energy of the complex and $E_A^{\{AB\}}$ and $E_B^{\{AB\}}$ are the monomer energies calculated using the full dimer basis set.[90] ΔE_{DCBS} is "free" from BSSE, and therefore, is the interaction energy at any given point. By inference, BSSE can be defined as:[90]

$$\mathbf{BSSE = \Delta E_{MCBS} - \Delta E_{DCBS}} \qquad \textbf{Equation 8}$$

In this study, the system being examined is a "trimer" composed of **31**, K^+ and picrate anion. However, the interaction of interest involves **31***K^+ and picrate anion. Accordingly, "monomers" A and B were defined as **31***K^+ and picrate anion, respectively. BSSE was quantified for each optimized point and then was subtracted from the total complex energy at that point.

Calculations were performed in collaboration with Dr. T. D. Power by using the Gaussian 98[79] program on the Linux cluster computer resources provided by the University of North Texas Academic Computing Services.

Results and Discussion

The initial potential energy surface (PES) for the movement of picrate along the axis of atoms 1 and 97 is shown in Figure 18. The first minimum is at distance, $r_{(1\text{-}97)}$ = 4.43 A. This distance is equal to the distance $r_{(1\text{-}97)}$ in the B3LYP/ 6-31G optimized geometry.

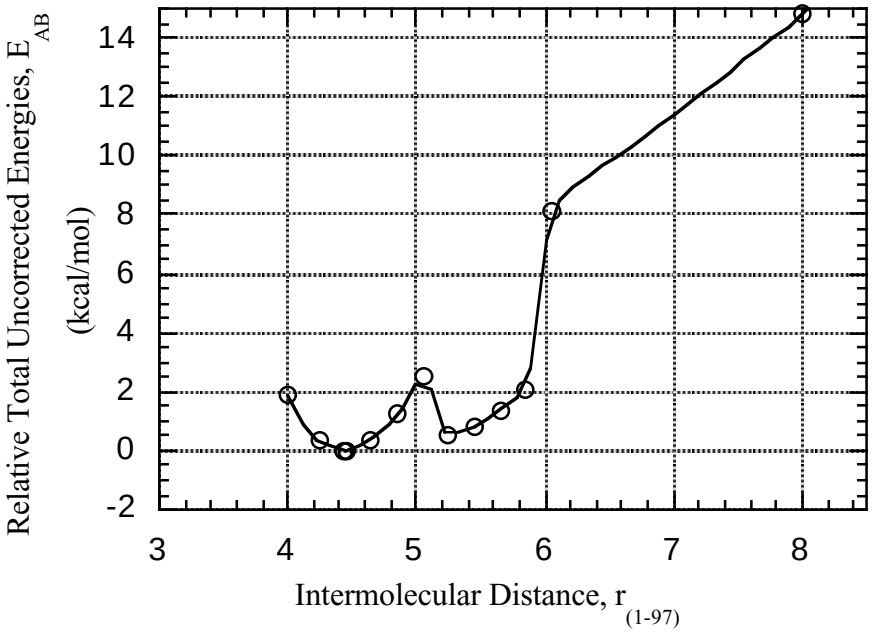


Figure 18. Potential energy surface for the interaction between picrate anion and **31***K^+.

The second minimum energy well on this PES occurring at approximately $r_{(1\text{-}97)}$ = *ca*. 5.3 A was unexpected. Further investigation of the geometries at $r_{(1\text{-}97)}$ = 5.25 and 5.45 A, revealed the picrate anion has rotated in an anti-clockwise direction so that interaction with the **31***K^+ complex now involves the phenoxide oxygen and an oxygen

on the other *o*-NO_2 located at C (atom 91). (Figure 19). Thus, while the distance $r_{(1\text{-}97)}$ is maintained at 5.25 and 5.45 A, the distance between the K^+ (atom 1) and picrate carbon (atom 91) is only 4.36 And 4.46 A, respectively.

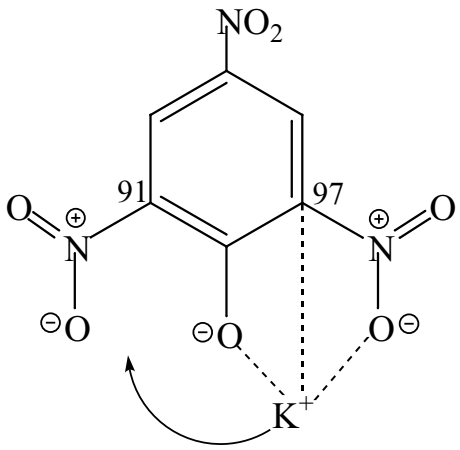


Figure 19. How picrate anion rotates around K^+.

Figure 20 shows the new PES obtained after correction for BSSE contamination has been applied at each point. Here, the minimum distance $r_{(1\text{-}97)}$, has shifted to 4.63 . This result is consistent with the fact that BSSE contamination causes the intermolecular interactions to appear artificially too attractive.[92] In fact, the contribution due to BSSE was found to be approximately 17% of ΔE_{MCBS} at the minimum energy geometry. The distance $r_{(1\text{-}97)}$ = 4.63 A also compares well with the corresponding distance that was obtained experimentally by X-ray crystallographic methods, i.e., 4.51 A.

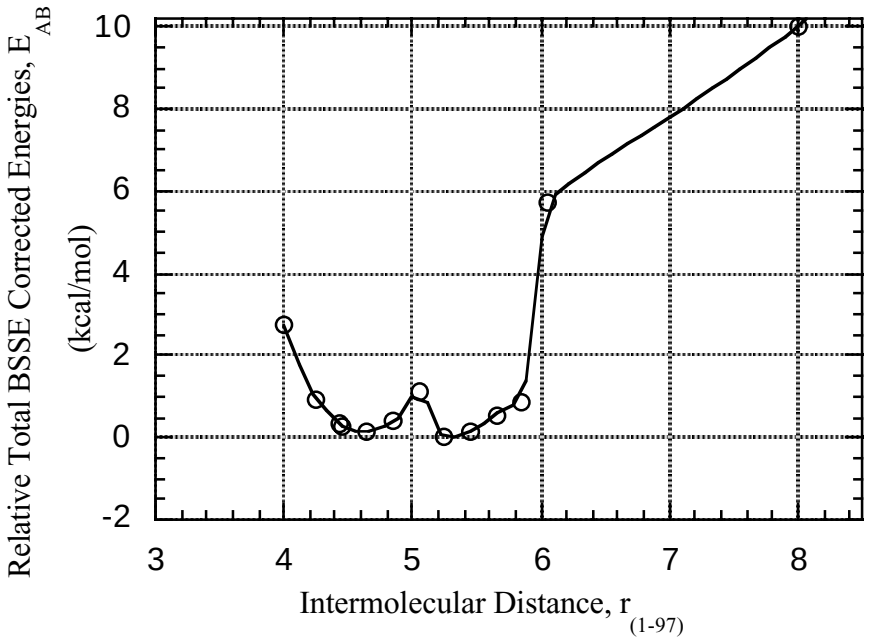


Figure 20. The BSSE corrected potential energy surface for the interaction between picrate anion and **31***K^+.

The interaction energy, ΔE_{DCBS}, at the minimum energy geometry was calculated to be -65.4 kcal/mol. This value respresents the stabilization energy contribution of picrate anion to the complex. However this result is only semi-quantitative; significantly higher level of theory would be required in order to obtain a more quantitative value. However, higher-level theoretical calculations are not practical for such a large system.

ΔE_{DCBS} for the minimum energy geometry was calculated at the Hartree-Fock (HF) and the Moller Plesset 2 (MP2) levels of theory for comparison. The results thereby obtained are shown in Table 11. The values obtained in this study by using B3LYP are much closer to the HF level and do not approach those obtained by using MP2 and higher

levels of theory. Thus, although the geometry obtained with B3LYP is of higher quality than that obtained by using HF, the same cannot be said for the calculated interaction energy.

Table 11. A comparison of ΔE_{DCBS} at HF, B3LYP and MP2 levels of theory.

Level of Theory	**ΔE_{DCBS} (kcal/mol)**
HF	-64.1
B3LYP	-65.4
MP2	-70.2

Complexation with other alkali metal picrates

After it had been established that the stabilization energy contribution from picrate anion indeed is significant, the next step was to determine whether incorporation of the counter ion in calculations could afford computational results that correlate well with experimental results. Thus, Na^+ was substituted for K^+ in the minimum energy structure and a geometry optimization with B3LYP/ 6-31G was carried out (Cartesian coordinates for the geometry obtained are listed in Appendix C). The interaction energy was defined as:

$$\Delta E = E_{ABC} - E_A^{\{ABC\}} - E_B^{\{ABC\}} - E_C^{\{ABC\}} \qquad \textbf{Equation 9}$$

where E_{ABC} is the energy of the complex and $E_A^{\{ABC\}}$, $E_B^{\{ABC\}}$ and $E_C^{\{ABC\}}$ are the monomer energies calculated using the full complex basis set. Here A, B, and C are defined as the crown ether **31**, the metal cation and the picrate anion, respectively. The preliminary results thereby obtained, shown in Table 12, reflect the trends observed in the

previous calculations, i.e., binding energy decreases with increasing cation size. Even though the interaction of the picrate anion has been shown to be significant, it does not affect the relative selectivities obtained via gas phase calculations.

Table 12. ΔE (kcal/mol) for complexes of Na^+ and K^+ picrate with compound **31**.

	Na^+	**K^+**
ΔE (kcal/mol)	-179.6	-153.1

Conclusions

The X-ray crystal structure of K^+ picrate-complexed **31** was obtained. It could be clearly ascertained that the picrate anion is intimately involved in stabilization of the complex. A computational study was undertaken to estimate the extent of the stabilization energy contribution from the picrate anion.

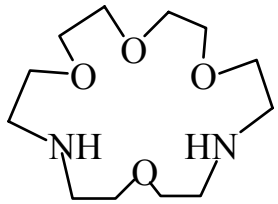
Counterpoise correction was performed to remove BSSE contamination from the computational results. BSSE was estimated to be 17% of the uncorrected interaction energy. The "BSSE-free" interaction energy is estimated to be -65.4 kcal/ mol at the B3LYP level of theory. At the minimum on the PES, the distance between K^+ (atom 1) and C (atom 97) is 4.63 A (Figure 17), which compares well with the corresponding distance of 4.51 A obtained via X-ray structural analysis.

Thus, the presence of the picrate anion has been found to affect the total energy of the complex. Further calculations are being performed to discern if neglect of the anion may have been a significant factor in the failure to correlate the results of previous

calculations (Chapter 3) with corresponding results of alkali metal picrate extraction experiments. However, preliminary results suggest that although the stabilization energy contribution from picrate anion is significant, it does not affect the relative selectivities obtained via gas phase calculations.

APPENDIX A

DATA FROM ALKALI METAL PICRATE EXTRACTION EXPERIMENTS



28

Alkali metal picrate extraction experiments were performed as detailed in the experimental section of Chapter 2. Data below is for experiments carried out without pH control and at pH 11-12. A summary of this data is shown in Table 4.

Li^+

	without pH control		
	Blank	**28**	**% Extraction**
	0.22839	0.17877	18.95457
	0.22540	0.18115	17.87560
	0.22424	0.17827	19.18125
	0.22279	0.17810	19.25832
	0.22653	0.17039	22.75365
	0.22313	0.16983	23.00753
Mean	**0.22508**		**20.172**
S. D.	**2.14×10^{-3}**		**2.158**

Na^+

	without pH control		
	Blank	**28**	**% Extraction**
	0.20854	0.15756	24.46064
	0.20644	0.15080	27.70160
	0.21083	0.16127	22.68194
	0.21068	0.15947	23.54492
	0.20712	0.15924	23.65519
	0.20789	0.15929	23.63122
Mean	**0.20858**		**24.279**
S. D.	**1.83×10^{-3}**		**1.769**

K^+

	without pH control		
	Blank	**28**	**% Extraction**
	0.22038	0.17105	22.10483
	0.22333	0.17160	21.85436
	0.21767	0.17134	21.97277
	0.21869	0.17508	20.26959
	0.21895	0.17149	21.90446
	0.21854	0.17137	21.95911
Mean	**0.21959**		**21.678**
S. D.	**2.03×10^{-3}**		**0.695**

Rb^+

	without pH control		
	Blank	**28**	**% Extraction**
	0.22040	0.17479	21.58719
	0.22458	0.17908	19.66264
	0.22527	0.17545	21.29110
	0.22505	0.17413	21.88327
	0.22305	0.17780	20.23687
	0.21912	0.17725	20.48360
Mean	**0.22291**		**20.857**
S. D.	**2.59×10^{-3}**		**0.863**

Cs^+

	without pH control		
	Blank	**28**	**% Extraction**
	0.21831	0.16370	25.26479
	0.22113	0.16570	24.35172
	0.21664	0.16211	25.99069
	0.21925	0.16861	23.02319
	0.21863	0.16562	24.38824
	0.22028	0.16803	23.28798
Mean	**0.21904**		**24.384**
S. D.	**1.58×10^{-3}**		**1.132**

Li^+

	pH 11-12		
	Blank	**28**	**% Extraction**
	0.17976	0.17693	1.72739
	0.17888	0.17540	2.57721
	0.18137	0.17278	4.03244
	0.17921	0.17369	3.52699
	0.18071	0.17648	1.97734
	0.18028	0.17342	3.67696
Mean	**0.18004**		**2.920**
S. D.	**9.37×10^{-4}**		**0.960**

Na^+

	pH 11-12		
	Blank	**28**	**% Extraction**
	0.17618	0.17360	2.39514
	0.17834	0.17360	2.39514
	0.17787	0.17221	3.17666
	0.17853	0.17145	3.60396
	0.17654	0.16714	6.02721
	0.17969	0.16899	4.98707
Mean	**0.17786**		**3.764**
S. D.	**1.31×10^{-3}**		**1.465**

K^+

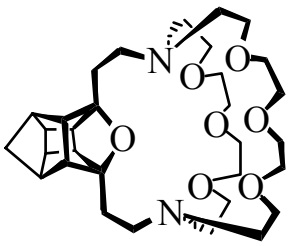
	pH 11-12		
	Blank	**28**	**% Extraction**
	0.18262	0.16409	10.27450
	0.18266	0.15912	12.99213
	0.18071	0.16255	11.11658
	0.18178	0.16505	9.74956
	0.18526	0.16023	12.38517
	0.18423	0.16238	11.20954
Mean	**0.18288**		**11.288**
S. D.	**1.64×10^{-3}**		**1.228**

Rb^+

	pH 11-12		
	Blank	**28**	**% Extraction**
	0.18187	0.17549	3.59811
	0.18114	0.17288	5.03186
	0.18324	0.17441	4.19139
	0.18414	0.17097	6.08108
	0.18103	0.16847	7.45441
	0.18082	0.16879	7.27862
Mean	**0.18204**		**5.606**
S. D.	**1.36×10^{-3}**		**1.600**

Cs^+

	pH 11-12		
	Blank	**28**	**% Extraction**
	0.18549	0.16377	(11.63330)
	0.18756	0.16249	(12.32396)
	0.18330	0.17912	3.35078
	0.18510	0.17819	3.85078
	0.18651	0.17896	3.43711
	0.18401	0.17772	4.10619
Mean	**0.18533**		**3.687**
S. D.	**1.57×10^{-3}**		**0.355**



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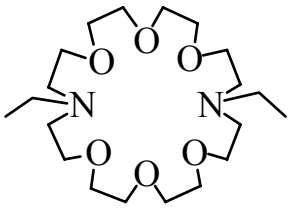


27

Alkali metal picrate extraction experiments were performed as detailed in the experimental section of Chapter 2. Data below is for experiments carried out at pH 11-12. A summary of this data is shown in Table 5.

Li^+

	Blank	**15**	**% Extraction**	**27**	**% Extraction**
	0.17976	0.17029	5.41546	0.16417	8.81471
	0.17888	0.16826	6.54299	0.16283	9.55899
	0.18137	0.17068	5.19884	0.16222	9.89780
	0.17921	0.17125	4.88225	0.16412	8.84248
	0.18071	0.16853	6.39302	0.16263	9.67007
	0.18028	0.16820	6.57632	0.16302	9.45345
Mean	**0.18004**		**5.835**		**9.373**
S. D.	**9.37×10^{-4}**		**0.755**		**0.447**

Na^+

	Blank	**15**	**% Extraction**	**27**	**% Extraction**
	0.17618	0.15343	13.73552	0.15944	10.35646
	0.17834	0.15392	13.46002	0.15825	11.02553
	0.17787	0.15581	12.39739	0.15796	11.18858
	0.17853	0.15401	13.40942	0.15685	11.81266
	0.17654	0.15620	12.17812	0.15871	10.76690
	0.17969	0.15538	12.63915	0.15721	11.61026
Mean	**0.17786**		**12.970**		**11.127**
S. D.	**1.31×10^{-3}**		**0.646**		**0.537**

K^+

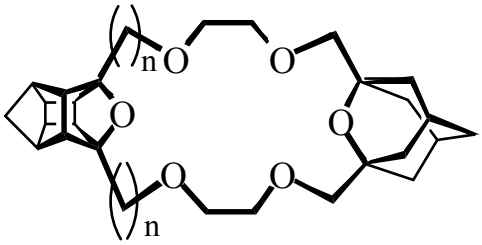
	Blank	15	% Extraction	27	% Extraction
	0.18262	0.12065	34.02778	0.15416	15.70429
	0.18266	0.11993	34.42148	0.15225	16.74869
	0.18071	0.11836	35.27997	0.14925	18.38911
	0.18178	0.12076	33.96763	0.14899	18.53128
	0.18526	0.11992	34.42695	0.14713	19.54833
	0.18423	0.12265	32.93416	0.14925	18.38911
Mean	**0.18288**		**34.176**		**17.885**
S. D.	**1.64×10^{-3}**		**0.768**		**1.396**

Rb^+

	Blank	15	% Extraction	27	% Extraction
	0.18187	0.086411	52.53186	0.15637	14.10130
	0.18114	0.086914	52.25555	0.15704	13.73325
	0.18324	0.088501	51.38376	0.15755	13.45309
	0.18414	0.087494	51.93694	0.15685	13.83762
	0.18103	0.089493	50.83883	0.15468	15.02966
	0.18082	0.088333	51.47605	0.15508	14.80993
Mean	**0.18204**		**51.737**		**14.161**
S. D.	**1.36×10^{-3}**		**0.623**		**0.627**

Cs^+

	Blank	15	% Extraction	27	% Extraction
	0.18549	0.085648	53.78622	0.15765	14.93552
	0.18756	0.088608	52.18907	0.15942	13.98047
	0.18330	0.088531	52.23062	0.15517	16.27367
	0.18510	0.088593	52.19716	0.15691	15.33481
	0.18651	0.083130	55.14488	0.15625	15.69093
	0.18401	0.084915	54.18730	0.15523	16.24130
Mean	**0.18533**		**53.289**		**15.409**
S. D.	**1.57×10^{-3}**		**1.267**		**0.871**



n=1 30
n=2 31

Alkali metal picrate extraction experiments were performed as detailed in the experimental section of Chapter 2. Data below is for experiments carried out with no pH control. A summary of this data is shown in Table 10.

Li^+

	Blank	**30**	**% Extraction**	**31**	**% Extraction**
	0.18152	0.17316	4.58978	0.18117	0.17632
	0.18048	0.17482	3.67513	0.18349	-1.10199
	0.18040	0.17055	6.02788	0.18216	-0.36917
	0.17871	0.17117	5.68626	0.18251	-0.56201
	0.18344	0.17256	4.92038	0.18210	-0.33611
	0.18436	0.17462	3.78533	0.18272	-0.67772
Mean	**0.18149**		**4.81**		**-0.478**
S. D.	**2.10×10^{-3}**		**0.964**		**0.423**

Na^+

	Blank	**30**	**% Extraction**	**31**	**% Extraction**
	0.18349	0.14899	19.95380	0.18581	0.17192
	0.18410	0.14893	19.98603	0.18556	0.30624
	0.18608	0.14520	21.99001	0.18304	1.66013
	0.18658	0.14638	21.35604	0.18596	0.09133
	0.18967	0.15033	19.23387	0.18236	2.02547
	0.18683	0.14891	19.99678	0.18419	1.04228
Mean	**0.18613**		**20.419**		**0.883**
S. D.	**2.21×10^{-3}**		**1.033**		**0.825**

K^+

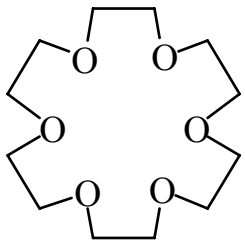
	Blank	30	% Extraction	31	% Extraction
	0.18814	0.049988	73.24413	0.15359	17.79157
	0.18822	0.052246	72.03554	0.15599	16.50698
	0.186107	0.054672	70.73703	0.15120	19.07081
	0.18596	0.059494	68.15608	0.15187	18.71220
	0.18506	0.053909	71.14543	0.15413	17.50254
	0.18755	0.052536	71.88032	0.15492	17.07970
Mean	**0.18683**		**71.200**		**17.778**
S. D.	**1.31×10^{-3}**		**1.722**		**0.972**

Rb^+

	Blank	30	% Extraction	31	% Extraction
	0.19202	0.068420	64.23793	0.16939	11.46247
	0.19005	0.06986	63.48526	0.17273	9.71670
	0.19147	0.070145	63.33630	0.17033	10.97115
	0.19066	0.069504	63.67134	0.17137	10.42756
	0.19196	0.069809	63.51192	0.16608	13.19256
	0.19186	0.069168	63.84696	0.16708	12.66987
Mean	**0.19132**		**63.682**		**11.407**
S. D.	**8.18×10^{-3}**		**0.324**		**1.326**

Cs^+

	Blank	30	% Extraction	31	% Extraction
	0.19055	0.093903	51.35568	0.18820	2.50725
	0.19569	0.092026	52.32801	0.18762	2.80771
	0.19255	0.093155	51.74316	0.18571	3.79714
	0.19397	0.094193	51.20545	0.18735	2.94758
	0.19339	0.089386	53.69561	0.18794	2.64194
	0.19211	0.088074	54.37526	0.18611	3.58993
Mean	**0.19304**		**52.450**		**3.049**
S. D.	**1.75×10^{-3}**		**1.305**		**0.525**



18-crown-6

Alkali metal picrate extraction experiments were performed as detailed in the experimental section of Chapter 2. Data below is for experiments carried out with no pH control. A summary of this data is shown in Table 10.

Li^+

	Blank	**18-crown-6**	**% Extraction**
	0.20001	0.19835	1.24471
	0.20068	0.20050	0.17426
	0.20096	0.19627	2.28031
	0.20184	0.19646	2.18571
	0.20047	0.19458	3.12173
	0.20114	0.20015	0.34852
Mean	**0.20085**		**1.559**
S. D.	**6.25×10^{-4}**		**1.169**

Na^+

	Blank	**18-crown-6**	**% Extraction**
	0.16986	0.15982	6.20342
	0.17020	0.16191	4.97682
	0.17097	0.16057	5.76325
	0.16911	0.16246	4.65403
	0.17123	0.16219	4.81249
	0.17096	0.16368	3.93802
Mean	**0.17039**		**5.058**
S. D.	**8.15×10^{-4}**		**0.812**

K^+

	Blank	18-crown-6	% Extraction
	0.17844	0.062088	65.23044
	0.17589	0.060608	66.05925
	0.17892	0.063095	64.66652
	0.17831	0.062714	64.87988
	0.18083	0.062073	65.23884
	0.17900	0.061844	65.36708
Mean	**0.17857**		**65.240**
S. D.	**1.58×10^{-3}**		**0.479**

Rb^+

	Blank	18-crown-6	% Extraction
	0.17825	0.090012	48.72864
	0.17310	0.089188	49.19799
	0.17542	0.090576	48.40738
	0.17416	0.090576	48.40738
	0.17793	0.089371	49.09376
	0.17448	0.087341	50.25006
Mean	**0.17556**		**49.01420**
S. D.	**2.10×10^{-3}**		**0.691**

Cs^+

	Blank	18-crown-6	% Extraction
	0.17957	0.13049	27.02310
	0.17752	0.12654	29.23215
	0.17810	0.12704	28.95252
	0.17812	0.12785	28.49952
	0.18092	0.12999	27.30272
	0.17860	0.12889	27.91790
Mean	**0.17881**		**28.155**
S. D.	**1.24×10^{-3}**		**0.892**

APPENDIX B

CARTESIAN COORDINATES AND ENERGIES OBTAINED FROM GEOMETRY OPTIMIZATIONS OF CAGE FUNCTIONALIZED CRYPTANDS AND THEIR ALKALI METAL COMPLEXES

Cartesian (x, y, z) coordinates and energies corresponding to stationary points obtained from geometry optimizations at the Hartree-Fock level of theory with 3-21G basis set and single-point energies obtained at other levels of theory (specified) with these geometries.

Cage-[1.1.1] cryptand (29)

E_h = -1217.39829743 a.u.

H	5.270353	-0.327761	1.343760
C	4.895723	-0.336828	0.326667
H	5.723368	-0.450534	-0.364236
C	4.008463	0.885549	0.001754
C	3.783047	-1.385877	0.106012
C	3.416581	0.523759	-1.379798
C	1.865268	0.675836	-1.294950
C	1.507356	1.106050	0.145591
C	2.784144	0.691889	0.920338
H	4.483037	1.853647	0.064194
C	0.585983	-2.398991	0.620847
H	3.927358	0.940108	-2.232947
H	1.354987	1.193815	-2.086918
H	1.092541	-1.350619	-1.969655
O	0.537301	0.103642	0.573641
C	1.031759	2.530570	0.392032
H	2.628907	-1.253933	2.002155
H	2.866432	1.158255	1.891415
C	3.260456	-1.044096	-1.308577
C	1.708445	-0.878783	-1.224256
C	1.289517	-1.099191	0.246803
C	2.629876	-0.871142	0.991581
H	4.059415	-2.418227	0.262420
H	3.672763	-1.628197	-2.115389
H	1.874330	3.187284	0.186775
H	0.803551	2.631836	1.446387
C	-0.161110	3.056826	-0.457867
N	-1.465833	2.426356	-0.331601
H	0.119728	3.023780	-1.503706
H	-0.274156	4.107523	-0.203306
C	-0.670413	-2.797973	-0.179237
H	0.365964	-2.380233	1.680642
H	1.312207	-3.193999	0.469823

H	-0.438746	-2.749324	-1.233660
N	-1.870390	-1.979989	0.047452
H	-0.874083	-3.847871	0.052202
C	-1.714651	1.177177	-1.064975
C	-2.201079	2.626379	0.913363
C	-2.913581	-2.207606	-0.974574
H	-3.474001	-2.047820	1.397318
H	-2.437825	-2.331260	-1.936194
C	-3.885240	-1.027954	-1.123998
H	-3.473888	-3.117990	-0.755256
H	-4.857963	-1.399291	-1.422559
O	-3.433708	-0.133787	-2.164498
H	-3.972711	-0.502060	-0.184309
H	-1.632920	0.315213	-0.434794
H	-0.969799	1.086602	-1.844038
C	-3.089052	1.199463	-1.730493
H	-3.089123	1.821087	-2.613837
H	-3.843559	1.572158	-1.050062
H	-1.956635	3.614650	1.290645
C	-1.946857	1.606624	2.029736
H	-3.264782	2.615202	0.712973
H	-0.889606	1.437774	2.144501
O	-2.598289	0.362947	1.685850
H	-2.353593	1.980374	2.965719
C	-1.983057	-0.806980	2.253590
H	-2.314027	-0.941258	3.280571
C	-2.392659	-2.019874	1.426606
H	-0.914717	-0.689494	2.234270
H	-2.065174	-2.925390	1.937022

HF/ 6-31G// HF/ 3-21G E_h = -1223.60326074 a.u.

Li^+-Cage-[1.1.1] cryptand (29•Li^+)

E_h = -1224.85224474 a.u.

H	-3.891785	-0.063841	2.663639
C	-4.187201	-0.024933	1.621931
H	-5.267984	-0.015536	1.553201
C	-3.545723	-1.142575	0.770953
C	-3.530606	1.141879	0.852530
C	-3.916846	-0.733856	-0.673119
C	-2.603025	-0.703810	-1.517473
C	-1.436643	-1.082001	-0.579522

C	-2.040717	-0.800682	0.814045
H	-3.794939	-2.156465	1.045534
C	-0.769056	2.509781	-0.703327
H	-4.783320	-1.218081	-1.090926
H	-2.586887	-1.176707	-2.485751
H	-2.570295	1.395126	-2.394390
Li	1.211908	0.026793	-0.052600
C	-0.801151	-2.431647	-0.879057
H	-1.484352	1.158145	1.720469
H	-1.503056	-1.247928	1.635656
C	-3.906672	0.842088	-0.616878
C	-2.592945	0.855122	-1.462028
C	-1.422887	1.150991	-0.499839
C	-2.030182	0.778876	0.870852
H	-3.766749	2.136613	1.199066
H	-4.766753	1.365802	-0.998698
H	-0.471105	-2.422460	-1.909904
H	-1.589791	-3.175309	-0.811580
C	0.335289	-2.894663	0.046685
N	1.580060	-2.083359	-0.032340
H	0.563413	-3.935649	-0.179459
H	-0.013219	-2.863739	1.068145
C	0.347803	2.906635	0.275949
H	-1.553398	3.254639	-0.604601
H	-0.420143	2.561198	-1.726693
H	0.563577	3.965281	0.138119
N	1.603615	2.112332	0.156522
H	-0.015691	2.781338	1.284140
C	2.310881	-2.279229	-1.305739
C	2.430571	-2.278221	1.166059
C	2.346486	2.409476	-1.088422
H	3.288108	2.854081	1.244984
H	1.636780	2.449525	-1.898396
C	3.363201	1.315377	-1.418194
H	2.854214	3.370297	-1.028487
H	3.715517	1.432560	-2.434802
O	2.656507	0.068979	-1.268754
H	4.216480	1.337929	-0.752260
H	1.592190	-2.236130	-2.107605
H	2.806685	-3.247403	-1.342411
C	3.338469	-1.168508	-1.544255
H	3.674035	-1.196120	-2.572964
H	4.203645	-1.260941	-0.900002
H	2.449392	-3.318851	1.481395

C	1.929393	-1.399108	2.312313
H	3.444187	-1.997108	0.924460
H	0.961004	-1.714557	2.662267
O	1.752503	-0.037887	1.847916
H	2.621818	-1.425414	3.145097
C	2.921313	0.816827	1.839543
H	3.667475	0.411525	1.173413
C	2.436850	2.194052	1.385103
H	3.337173	0.881456	2.837360
H	1.833318	2.602757	2.181570
O	-0.500336	0.036354	-0.759128

HF/ 6-31G// HF/ 3-21G E_h = -1231.06697434 a.u.

Na^+-cage-[1.1.1] cryptand (29•Na^+)

E_h = -1378.264.90892 a.u.

H	3.318494	-0.000001	2.959227
C	3.826352	0.000000	2.001885
H	4.897436	0.000000	2.161566
C	3.362971	1.142687	1.072723
C	3.362972	-1.142687	1.072723
C	4.033391	0.788436	-0.274928
C	2.926366	0.784823	-1.376765
C	1.580507	1.120333	-0.693261
C	1.887422	0.788890	0.786732
H	3.532801	2.148486	1.426339
C	0.924504	-2.455837	-1.049654
H	4.962170	1.292651	-0.482089
H	3.107457	1.288487	-2.312005
H	3.107459	-1.288487	-2.312004
Na	-0.952179	0.000002	0.076938
C	0.924502	2.455838	-1.049652
H	1.185033	-1.198377	1.498005
H	1.185032	1.198375	1.498006
C	4.033393	-0.788433	-0.274928
C	2.926368	-0.784822	-1.376765
C	1.580508	-1.120331	-0.693262
C	1.887423	-0.788890	0.786732
H	3.532804	-2.148485	1.426337
H	4.962173	-1.292645	-0.482089
H	0.533796	2.362350	-2.055009
H	1.706437	3.208453	-1.083052

C	-0.153793	3.015660	-0.084075
N	-1.410086	2.211316	0.049345
H	-0.396446	4.024731	-0.411830
H	0.283128	3.105611	0.899083
C	-0.153791	-3.015660	-0.084076
H	1.706438	-3.208451	-1.083056
H	0.533796	-2.362347	-2.055010
H	-0.396443	-4.024731	-0.411832
N	-1.410083	-2.211316	0.049345
H	0.283131	-3.105611	0.899081
C	-2.278729	2.379089	-1.144255
C	-2.068418	2.405461	1.367650
C	-2.278727	-2.379089	-1.144255
H	-2.684888	-3.303185	1.377010
H	-1.625655	-2.420446	-2.001907
C	-3.284963	-1.244420	-1.409396
H	-2.826178	-3.319335	-1.093957
H	-3.692168	-1.375889	-2.404616
O	-2.570703	0.000000	-1.319267
H	-4.107247	-1.255137	-0.708349
H	-1.625657	2.420449	-2.001906
H	-2.826181	3.319335	-1.093956
C	-3.284963	1.244420	-1.409397
H	-3.692167	1.375888	-2.404619
H	-4.107249	1.255136	-0.708351
H	-1.284308	2.540231	2.099007
C	-2.941108	1.233192	1.857702
H	-2.684895	3.303180	1.377009
H	-3.244823	1.440678	2.875853
O	-2.180144	-0.000002	1.816596
H	-3.830648	1.122230	1.257574
C	-2.941107	-1.233197	1.857704
H	-3.830648	-1.122236	1.257578
C	-2.068414	-2.405463	1.367650
H	-3.244820	-1.440683	2.875855
H	-1.284303	-2.540229	2.099006
O	0.744133	0.000000	-1.129711

HF/ 6-31G// HF/ 3-21G E_h = -1385.40599495 a.u.

K^+-cage-[1.1.1] cryptand (29•K^+)

E_h = -1813.4511186 a.u.

H	5.363099	0.094207	-1.647023
C	5.033150	-0.053051	-0.625549
H	5.894157	-0.201697	0.014551
C	3.986217	-1.180357	-0.486259
C	4.104158	1.074039	-0.123392
C	3.509040	-1.030368	0.975477
C	1.949464	-0.940812	0.970522
C	1.473263	-1.015391	-0.493486
C	2.769711	-0.635067	-1.261177
H	4.308484	-2.170572	-0.771590
C	1.006714	2.622687	-0.163807
H	3.981817	-1.681170	1.692217
H	1.395941	-1.514944	1.685711
H	1.508022	0.966505	2.081081
O	0.676978	0.189756	-0.661014
C	0.727243	-2.257521	-1.003173
H	2.876896	1.498402	-1.928033
H	2.747064	-0.895233	-2.310684
C	3.589093	0.524622	1.226380
C	2.028109	0.598196	1.217893
C	1.589713	1.186310	-0.146098
C	2.852776	0.925797	-1.011572
H	4.528858	2.066034	-0.089306
H	4.114382	0.867335	2.102234
H	1.462958	-3.052746	-1.083903
H	0.395179	-2.069224	-2.022357
C	-0.432845	-2.852917	-0.150262
N	-1.660522	-2.031980	0.041952
H	-0.031105	-3.073810	0.825519
H	-0.638198	3.937742	-0.483164
H	-0.694586	-3.812992	-0.593283
C	-0.480693	2.862948	-0.578970
H	1.581813	3.214155	-0.869428
H	1.179237	3.074040	0.803588
N	-1.538088	2.113247	0.149033
H	-0.575468	2.646517	-1.639040
C	-2.208508	-2.104266	1.415335
C	-2.737287	-2.284553	-0.934758
C	-1.375013	2.122065	1.620560
H	-3.459399	2.796453	0.641722
H	-0.330698	2.160874	1.862387

C	-1.926026	0.871811	2.287619
H	-1.850456	3.004575	2.046289
H	-2.105777	1.067688	3.340057
O	-0.913189	-0.144954	2.159171
H	-2.842653	0.568495	1.814390
H	-2.409319	-3.137751	1.702303
H	-3.147486	-1.579230	1.411649
C	-1.318642	-1.474862	2.485774
H	-0.411542	-2.038367	2.625672
H	-1.861619	-1.497982	3.427398
H	-2.304305	-2.315716	-1.930141
C	-3.877136	-1.204574	-0.877164
H	-3.205613	-3.257085	-0.786413
H	-4.291073	-1.072103	-1.873985
O	-3.346087	0.042081	-0.369271
H	-4.676923	-1.533701	-0.232104
C	-3.787359	1.312444	-0.880222
H	-4.829976	1.488077	-0.650158
C	-2.931818	2.457216	-0.240237
H	-3.698734	1.327317	-1.967373
H	-2.935986	3.290231	-0.937496
K	-1.328856	0.127651	-1.893151

HF/ 6-31G// HF/ 3-21G E_h = -1822.60270385 a.u.

Rb^+-cage-[1.1.1] cryptand (29•Rb^+)

E_h = -4142.01374497 a.u.

H	-4.810422	-1.273853	-1.739534
C	-4.784290	-0.721119	-0.807690
H	-5.794965	-0.575530	-0.446789
C	-3.993956	0.601776	-0.911275
C	-3.860610	-1.362713	0.250414
C	-3.900750	1.065995	0.558806
C	-2.399663	1.352036	0.884759
C	-1.565166	1.036966	-0.375596
C	-2.548264	0.133348	-1.175071
H	-4.371914	1.334664	-1.608095
C	-0.671673	-1.978403	1.465497
H	-4.637491	1.787925	0.869081
H	-2.152468	2.262579	1.403025
H	-1.981068	0.046165	2.702067
O	-0.573680	0.083534	0.091366

C	-0.902622	2.199855	-1.109485
H	-2.165338	-2.077411	-0.985010
H	-2.313403	0.038942	-2.229684
C	-3.809314	-0.287878	1.361399
C	-2.310532	0.007618	1.678056
C	-1.442400	-0.873732	0.748504
C	-2.454388	-1.231711	-0.372952
H	-4.124206	-2.356832	0.577955
H	-4.490057	-0.433434	2.183191
H	-1.677836	2.915446	-1.366565
H	-0.483270	1.864649	-2.053418
C	0.176589	2.952258	-0.299107
N	1.414121	2.199526	0.012360
H	-0.268980	3.256042	0.635921
H	0.599106	-3.678905	1.118925
H	0.421109	3.871376	-0.832804
C	0.479112	-2.678756	0.701054
H	-1.391531	-2.733006	1.766119
H	-0.260001	-1.530593	2.353527
N	1.757837	-1.934433	0.757939
H	0.205733	-2.819411	-0.339461
C	1.911650	2.500677	1.368666
C	2.441531	2.284501	-1.037799
C	2.289134	-1.741068	2.123699
H	3.384439	-3.181790	0.164564
H	1.624404	-2.191713	2.846465
C	2.467537	-0.270474	2.479548
H	3.248051	-2.244618	2.226713
H	2.916754	-0.184080	3.465643
O	1.181742	0.350868	2.456122
H	3.126793	0.187558	1.763572
H	1.858060	3.570643	1.576227
H	2.955702	2.240588	1.426530
C	1.149406	1.783388	2.493031
H	0.103365	2.036768	2.459337
H	1.554046	2.141263	3.436849
H	1.956131	2.166326	-1.999904
C	3.561374	1.233517	-0.933965
H	2.924673	3.264018	-1.055177
H	4.300677	1.446316	-1.698079
O	3.036202	-0.097264	-1.127509
H	4.053024	1.295122	0.025200
C	3.762667	-1.203943	-0.548285
H	4.280729	-0.882188	0.343289

C	2.788548	-2.345053	-0.202197
H	4.503169	-1.565859	-1.252602
H	2.313379	-2.692165	-1.112800
Rb	0.673846	-0.664872	-2.200440

HF/ 6-31G// HF/ 3-21G E_h = -4148.21312033 a.u.

Cs^+-cage-[1.1.1] cryptand (29•Cs^+)

E_h = -8747.38068681 a.u.

H	-4.777607	-2.068277	0.524055
C	-4.785010	-0.995359	0.370904
H	-5.807667	-0.638535	0.372825
C	-4.005336	-0.558575	-0.888983
C	-3.886640	-0.235569	1.371136
C	-3.960685	0.978512	-0.753297
C	-2.473323	1.435630	-0.887655
C	-1.594340	0.179467	-1.077057
C	-2.547637	-0.935503	-0.555153
H	-4.370113	-0.932173	-1.833987
C	-0.755736	0.765826	2.423062
H	-4.712962	1.519355	-1.302861
H	-2.255097	2.270654	-1.529766
H	-2.093148	2.625557	1.011285
O	-0.605180	0.265494	-0.015559
C	-0.930766	-0.011180	-2.436087
H	-2.146649	-1.594212	1.561427
H	-2.282709	-1.937091	-0.872853
C	-3.879453	1.203741	0.805088
C	-2.393709	1.656000	0.654257
C	-1.488805	0.488211	1.113991
C	-2.463838	-0.715495	1.013553
H	-4.149841	-0.322708	2.414334
H	-4.582921	1.885231	1.253223
H	-1.713199	-0.045000	-3.188405
H	-0.425438	-0.969721	-2.479275
C	0.055954	1.108146	-2.834188
N	1.283834	1.207894	-2.018055
H	-0.466031	2.050391	-2.766382
H	0.570495	-0.117444	3.862933
H	0.310289	0.977986	-3.887056
C	0.461736	-0.116375	2.777459
H	-1.483868	0.686422	3.224072

H	-0.422661	1.787989	2.372161
N	1.710027	0.325572	2.124807
H	0.270924	-1.144261	2.490616
C	1.684310	2.604151	-1.771999
C	2.365395	0.328595	-2.481070
C	2.135058	1.699857	2.448995
H	3.422434	-0.572835	3.023884
H	1.438002	2.152950	3.139299
C	2.239906	2.583424	1.211738
H	3.101697	1.685592	2.948978
H	2.629492	3.559449	1.490235
O	0.939288	2.707679	0.633132
H	2.923069	2.130201	0.515927
H	1.585029	3.209214	-2.674834
H	2.730305	2.630115	-1.512841
C	0.871771	3.302433	-0.669750
H	-0.175346	3.302151	-0.920479
H	1.207932	4.335759	-0.626056
H	1.934217	-0.634463	-2.726119
C	3.494532	0.096384	-1.465831
H	2.830566	0.701162	-3.396762
H	4.274040	-0.483736	-1.948822
O	3.005283	-0.612413	-0.309106
H	3.930621	1.036489	-1.161770
C	3.749919	-0.464656	0.917970
H	4.215550	0.509886	0.956631
C	2.810986	-0.638236	2.122493
H	4.538820	-1.208207	0.966155
H	2.402801	-1.641182	2.107815
Cs	0.757293	-2.489521	-0.237819

HF/ 6-31G// HF/ 3-21G E_h = -8753.5860439 a.u.

Cage-[2.2.2] cryptand (9)

E_h = -1521.533312404 a.u.

H	-5.431633	-1.139567	-2.281538
C	-5.183425	-1.336292	-1.244903
H	-6.004724	-1.859134	-0.767747
C	-4.757183	-0.064506	-0.477916
C	-3.831474	-2.065454	-1.078989
C	-4.235550	-0.629428	0.863498
C	-2.806353	-0.048175	1.108736

C	-2.445725	0.852121	-0.094742
C	-3.441665	0.345277	-1.171240
H	-5.498260	0.717091	-0.395628
C	-0.366269	-1.905857	-1.159534
H	-4.940123	-0.626250	1.679709
H	-2.565324	0.338939	2.083129
H	-1.518787	-1.902975	1.398605
O	-1.177783	0.316098	-0.556408
C	-2.426368	2.363770	0.081825
H	-2.577785	-1.098865	-2.642045
H	-3.559212	1.027986	-2.000515
C	-3.595240	-2.010005	0.448500
C	-2.171901	-1.416585	0.694780
C	-1.552862	-1.087788	-0.683468
C	-2.804300	-1.032949	-1.588039
H	-3.756398	-3.046414	-1.524282
H	-3.890228	-2.887732	1.000680
C	-1.603993	2.922799	1.258325
H	-3.454169	2.687339	0.224518
H	-2.082225	2.797514	-0.848806
H	-1.936999	2.444277	2.169992
H	-1.846928	3.984497	1.359538
N	-0.158161	2.723190	1.145885
C	0.511589	3.396957	0.023445
C	0.558684	2.796209	2.422078
H	-0.114343	-1.593842	-2.163992
H	-0.640964	-2.955052	-1.202270
C	0.851564	-1.725183	-0.237187
H	1.019821	-0.673543	-0.053283
N	2.062789	-2.363064	-0.805950
H	0.650765	-2.163353	0.724061
H	3.352224	-0.680884	-0.672391
H	3.316106	-4.018549	-0.604496
H	0.141439	3.576003	3.061603
H	1.592624	3.046909	2.232871
C	0.573908	1.476875	3.194209
H	-0.369287	0.956401	3.096362
H	0.741688	1.688472	4.247858
O	1.650636	0.653651	2.699383
C	1.995379	-0.423644	3.587067
H	2.313241	-0.019127	4.543994
C	3.124167	-1.232375	2.972862
H	1.152877	-1.083729	3.751819
H	3.812329	-0.556449	2.480561

O	2.542007	-2.149538	2.038744
H	3.654906	-1.772927	3.750605
C	3.448169	-2.908784	1.222835
H	3.860478	-3.741932	1.784623
H	4.271373	-2.283774	0.894580
C	2.654568	-3.420711	0.013895
H	1.860071	-4.063798	0.368539
H	-0.214706	3.854379	-0.633490
C	1.308597	2.371142	-0.764974
H	1.174409	4.186036	0.364139
O	2.043722	3.099014	-1.773641
H	0.621564	1.662408	-1.200414
H	1.973726	1.838527	-0.096725
C	2.460309	2.343770	-2.919174
C	3.636100	1.395215	-2.599343
H	2.749546	3.072585	-3.661614
H	1.636259	1.764718	-3.318573
H	3.726619	1.305391	-1.526296
H	4.564158	1.792549	-2.981534
O	3.488893	0.106645	-3.228485
C	2.502675	-0.771506	-2.647979
C	3.045884	-1.441923	-1.386642
H	2.286043	-1.525760	-3.388296
H	1.594230	-0.231361	-2.425416
H	3.927713	-2.002648	-1.672275

HF/ 6-31G// HF/ 3-21G E_h = -1529.29529049 a.u.

Li^+-cage-[2.2.1] cryptand (9•Li^+)

E_h = -1528.98415914 a.u.

H	-5.094243	0.680348	2.168736
C	-5.118603	0.237423	1.180279
H	-6.144504	0.026440	0.904202
C	-4.199692	-0.996980	1.049630
C	-4.377257	1.084087	0.122491
C	-4.225068	-1.282887	-0.469064
C	-2.748769	-1.371737	-0.966488
C	-1.826842	-1.126129	0.248421
C	-2.783431	-0.407968	1.228164
H	-4.432917	-1.837900	1.684773
C	-1.450379	2.184459	-1.263255
H	-4.919854	-2.039266	-0.793748

H	-2.483802	-2.184351	-1.619015
H	-2.644277	0.165571	-2.645127
Li	1.107969	0.451546	-0.025963
C	-1.092915	-2.321265	0.841470
H	-2.643572	1.807619	1.284282
H	-2.420543	-0.396994	2.245848
C	-4.345380	0.153166	-1.109387
C	-2.863294	0.051119	-1.595348
C	-1.996810	0.907700	-0.646044
C	-2.909122	1.023648	0.594759
H	-4.762825	2.076942	-0.053651
H	-5.116012	0.315479	-1.844110
C	-0.308944	-3.191843	-0.157556
H	-1.853363	-2.935361	1.314804
H	-0.423490	-1.966610	1.614198
H	-0.804112	-3.190918	-1.116198
H	-0.316977	-4.224506	0.184859
N	1.086088	-2.740369	-0.343002
C	2.005336	-3.425537	0.575390
C	1.508570	-2.676476	-1.748128
H	-2.298270	2.718556	-1.681495
H	-0.798243	1.919022	-2.086342
C	-0.722216	3.120420	-0.292715
H	-0.720454	4.130479	-0.697223
N	0.678212	2.703583	-0.008320
H	-1.263576	3.165949	0.638545
H	2.142255	3.062933	1.456590
H	1.507581	4.347064	-1.083715
H	1.138129	-3.524370	-2.323378
H	2.587170	-2.704916	-1.801025
C	1.019231	-1.380603	-2.388292
H	-0.026557	-1.226702	-2.201501
H	1.201868	-1.383199	-3.456678
O	1.686667	-0.239303	-1.786332
C	2.966534	0.132771	-2.350224
H	3.425809	-0.709996	-2.851654
C	3.851608	0.580040	-1.199506
H	2.813811	0.921757	-3.074513
H	4.067871	-0.242429	-0.547667
O	3.128632	1.513985	-0.369072
H	4.767502	1.023510	-1.571294
C	3.043279	2.882311	-0.819906
H	3.589765	3.020478	-1.745506
H	3.504235	3.508017	-0.071320

C	1.579703	3.260787	-1.041289
H	1.248925	2.870604	-1.993228
H	1.506898	-3.495575	1.532955
C	3.328110	-2.688749	0.762803
H	2.222483	-4.445746	0.253951
O	3.136986	-1.311149	1.128312
H	3.899848	-2.670514	-0.151403
H	3.920800	-3.202143	1.514130
C	2.816666	-1.055051	2.505666
C	2.505173	0.419015	2.621552
H	3.662820	-1.305338	3.136636
H	1.955270	-1.625535	2.821924
H	3.273206	0.994295	2.133091
H	2.429128	0.695793	3.665963
O	1.225568	0.653569	1.974328
C	0.577409	1.907914	2.309495
C	1.069172	3.016987	1.386999
H	0.777806	2.155296	3.345552
H	-0.477173	1.734090	2.189668
H	0.670626	3.975886	1.710188
O	-0.947288	-0.032178	-0.213919

HF/ 6-31G// HF/ 3-21G E_h = -1536.7456214 a.u.

Na^+-[2.2.1] cryptand (9•Na^+)

E_h = -1682.43018983 a.u.

H	5.053445	-0.001110	2.071498
C	5.065355	-0.037626	0.988584
H	6.090479	-0.040744	0.638756
C	4.216037	1.076750	0.338793
C	4.236362	-1.207897	0.415350
C	4.197581	0.674687	-1.153283
C	2.707544	0.634303	-1.623287
C	1.823782	1.003611	-0.408096
C	2.778409	0.721995	0.773244
H	4.519954	2.092333	0.543104
C	1.146355	-2.566810	-0.286131
H	4.921437	1.165288	-1.782163
H	2.431376	1.112297	-2.549220
H	2.485030	-1.461214	-2.475910
O	0.878311	-0.118262	-0.340667
C	1.129361	2.352057	-0.546560

H	2.473422	-1.254489	1.775137
H	2.481517	1.160855	1.711630
C	4.213514	-0.901479	-1.099886
C	2.726701	-0.923937	-1.574706
C	1.846731	-1.222120	-0.344111
C	2.789750	-0.854710	0.822038
H	4.560323	-2.202095	0.683374
H	4.948040	-1.418143	-1.694708
C	0.494293	2.953471	0.721620
H	0.378068	2.238860	-1.312230
H	1.879768	3.050634	-0.904367
H	0.536675	4.040363	0.662962
H	1.084779	2.680501	1.581222
Na	-1.224656	-0.268931	0.351432
C	-1.209550	2.527841	2.428308
C	-1.894961	3.448061	0.324952
H	0.579512	-2.623934	0.634044
H	1.909211	-3.336908	-0.263957
C	0.189330	-2.792603	-1.482327
H	0.412001	-2.081303	-2.262278
N	-1.224611	-2.596807	-1.094205
H	0.330829	-3.787055	-1.901896
H	-2.253456	-4.451354	-0.872973
H	-3.112599	-2.574619	-1.992497
H	-1.852243	4.431842	0.796219
H	-2.881448	3.044388	0.504972
C	-1.705481	3.677272	-1.170460
H	-0.753070	4.138348	-1.374237
H	-2.478926	4.361158	-1.505665
O	-1.748913	2.466551	-1.944731
C	-3.023744	2.046042	-2.456447
H	-3.719920	2.876587	-2.507665
C	-3.630370	0.941197	-1.598455
H	-2.850520	1.697048	-3.462834
H	-3.906860	1.312369	-0.624927
O	-2.701977	-0.132461	-1.344004
H	-4.517277	0.556475	-2.089541
C	-2.126995	-0.783014	-2.511065
H	-1.139715	-0.378525	-2.674613
H	-2.741414	-0.593438	-3.382488
C	-2.102388	-2.275516	-2.234579
H	-1.803221	-2.813155	-3.132570
H	-0.833646	3.431715	2.905710
C	-0.660102	1.305560	3.138649

H	-2.282316	2.504722	2.556791
O	-1.394831	0.166913	2.642045
H	-0.828198	1.411396	4.204560
H	0.396593	1.159846	2.966728
C	-1.422269	-0.986650	3.506612
C	-2.423460	-1.936727	2.894301
H	-1.728265	-0.700279	4.505297
H	-0.446015	-1.451688	3.544345
H	-3.387578	-1.450788	2.812522
H	-2.519440	-2.833131	3.494599
O	-1.903206	-2.250399	1.591561
C	-2.692623	-3.158023	0.791849
C	-1.751234	-3.700041	-0.268117
H	-3.526354	-2.622736	0.356343
H	-3.068750	-3.966981	1.407898
H	-0.930545	-4.182424	0.241257
N	-0.915689	2.534583	0.972441

HF/ 6-31G// HF/ 3-21G E_h = -1691.12970464 a.u.
HF/ 6-311G// HF/ 3-21G E_h = -1691.45884740 a.u.

K^+-cage-[2.2.1] cryptand (9•K^+)

E_h = -2117.70060176 a.u.

H	5.870104	0.187802	-1.544703
C	5.355110	0.291237	-0.597414
H	6.071866	0.525669	0.180395
C	4.477135	-0.932418	-0.254070
C	4.184814	1.297548	-0.656430
C	3.683793	-0.452828	0.984082
C	2.167514	-0.696451	0.701822
C	2.041269	-1.305083	-0.707996
C	3.389654	-0.904759	-1.350014
H	4.992303	-1.874004	-0.138291
C	1.002164	2.049801	-1.760524
H	4.085467	-0.744890	1.940527
H	1.535707	-1.124404	1.459703
H	1.222788	1.321108	1.013479
O	1.082435	-0.412300	-1.368889
C	1.705036	-2.784141	-0.852886
H	3.320235	0.888877	-2.666170
H	3.626877	-1.471286	-2.238486
C	3.481826	1.087327	0.705320

C	1.968460	0.828316	0.422654
C	1.756368	0.871544	-1.106723
C	3.189783	0.624345	-1.627600
H	4.440942	2.319528	-0.892929
H	3.752085	1.781898	1.484457
C	0.653259	-3.364622	0.109483
H	2.621158	-3.336743	-0.665712
H	1.436840	-2.967927	-1.885008
H	0.991761	-3.197141	1.119267
H	0.623656	-4.445550	-0.044855
K	-1.163698	0.018190	0.025573
C	-1.232992	-3.061962	-1.389567
C	-1.607666	-3.194760	1.068199
H	0.193436	1.632022	-2.346159
H	1.678118	2.526752	-2.460219
C	0.464747	3.152447	-0.817442
H	1.139883	3.276111	0.015163
N	-0.904362	2.873232	-0.293749
H	0.457304	4.099999	-1.353954
H	-2.016266	4.320508	-1.386944
H	-2.245011	3.530323	1.166336
H	-1.716944	-4.277949	1.146072
H	-2.574402	-2.766832	0.859522
C	-1.173343	-2.671972	2.441553
H	-0.282776	-3.160958	2.808939
H	-1.979176	-2.876279	3.138399
O	-0.934312	-1.246552	2.361752
C	-1.200126	-0.485852	3.559057
H	-2.264760	-0.318925	3.657837
C	-0.472220	0.841868	3.455502
H	-0.838976	-1.012224	4.435022
H	-0.650703	1.415149	4.358299
O	-0.969506	1.557513	2.304310
H	0.590904	0.668648	3.351281
C	-0.513564	2.925076	2.198597
H	0.564889	2.951700	2.123844
H	-0.803027	3.476201	3.086870
C	-1.182423	3.565569	0.986987
H	-0.888838	4.614159	0.940324
H	-0.706831	-2.405746	-2.066623
C	-2.731421	-2.831925	-1.577270
H	-1.036151	-4.092564	-1.688685
O	-3.080212	-1.513900	-1.104831
H	-3.325783	-3.572796	-1.059689

H	-2.942531	-2.913163	-2.638178
C	-4.214211	-0.902284	-1.748043
C	-4.409641	0.462029	-1.120249
H	-5.105664	-1.503029	-1.609349
H	-4.018784	-0.788742	-2.806316
H	-4.594942	0.361785	-0.057054
H	-5.256028	0.956082	-1.583527
O	-3.199134	1.211167	-1.341840
C	-3.294000	2.626341	-1.087468
C	-1.916890	3.237304	-1.320232
H	-3.652506	2.799606	-0.081205
H	-3.998292	3.074067	-1.779753
H	-1.574496	2.876578	-2.278274
N	-0.704487	-2.801323	-0.029041

HF/ 6-31G// HF/ 3-21G E_h = -2128.3917317 a.u.

Rb^+-cage-[2.2.1] cryptand (9•Rb^+)

E_h = -4446.22530906 a.u.

H	5.820131	-0.112232	-1.907238
C	5.390345	-0.074023	-0.913691
H	6.183990	-0.035951	-0.177213
C	4.382830	-1.215111	-0.650182
C	4.363052	1.067600	-0.747066
C	3.747800	-0.810126	0.700394
C	2.196504	-0.825867	0.522332
C	1.892139	-1.221923	-0.938351
C	3.235945	-0.907032	-1.637180
H	4.774325	-2.220301	-0.695058
C	1.278118	2.357723	-1.484174
H	4.171534	-1.274787	1.575727
H	1.573226	-1.263725	1.280506
H	1.553560	1.236340	1.165823
O	1.023040	-0.133370	-1.401669
C	1.339559	-2.613181	-1.270121
H	3.313462	1.040101	-2.709431
H	3.333658	-1.373498	-2.606459
C	3.734340	0.766344	0.633610
C	2.183399	0.737594	0.452724
C	1.873666	1.009029	-1.035009
C	3.222625	0.656662	-1.704047
H	4.736052	2.072501	-0.876930

H	4.148506	1.311194	1.466440
C	0.495196	-3.345983	-0.205502
H	2.195774	-3.255486	-1.451289
H	0.809632	-2.531410	-2.209554
H	1.018747	-3.283372	0.733644
H	0.462558	-4.402233	-0.477969
Rb	-1.243762	0.055583	0.188343
C	-1.729340	-3.231711	-1.174317
C	-1.481761	-3.278227	1.275918
H	0.550664	2.141413	-2.255287
H	2.078137	2.919065	-1.954119
C	0.674098	3.289771	-0.408640
H	1.295496	3.259741	0.471496
N	-0.729193	2.967730	-0.025732
H	0.718829	4.312849	-0.781730
H	-1.817778	4.543953	-0.947158
H	-2.165774	3.365652	1.438995
H	-1.565191	-4.365369	1.330811
H	-2.478109	-2.866614	1.334270
C	-0.741052	-2.811298	2.536182
H	0.230273	-3.270342	2.637072
H	-1.340973	-3.111180	3.388292
O	-0.575792	-1.373047	2.521730
C	-0.872622	-0.655752	3.740673
H	-1.943636	-0.550781	3.855740
C	-0.224030	0.717004	3.667156
H	-0.471308	-1.182053	4.598565
H	-0.380530	1.230423	4.609397
O	-0.822952	1.465656	2.588240
H	0.838933	0.605070	3.496983
C	-0.410867	2.847494	2.498401
H	0.665914	2.907151	2.419875
H	-0.710377	3.373472	3.398447
C	-1.103235	3.509459	1.305031
H	-0.905565	4.580929	1.355506
H	-1.269659	-2.815317	-2.058491
C	-3.196254	-2.784709	-1.143353
H	-1.735127	-4.317617	-1.286547
O	-3.357199	-1.349612	-1.111972
H	-3.715953	-3.172029	-0.282681
H	-3.679187	-3.191353	-2.025541
C	-3.585505	-0.692551	-2.380158
C	-3.991795	0.740813	-2.086734
H	-4.383128	-1.194439	-2.914426

H	-2.687871	-0.694771	-2.984423
H	-4.746469	0.739203	-1.309828
H	-4.395664	1.204175	-2.978815
O	-2.811872	1.447966	-1.655934
C	-3.017082	2.775753	-1.132346
C	-1.659272	3.473070	-1.072555
H	-3.498443	2.721361	-0.162783
H	-3.659826	3.340340	-1.799203
H	-1.200221	3.318627	-2.036133
N	-0.888812	-2.845009	-0.010713

HF/ 6-31G// HF/ 3-21G E_h = -4453.96041965 a.u.

Cs^+-cage-[2.2.1] cryptand (9•Cs^+)

E_h = -9051.56316819 a.u.

H	-5.739778	-0.175734	-2.043586
C	-5.344257	-0.225712	-1.036342
H	-6.155292	-0.387941	-0.336510
C	-4.473699	0.997075	-0.671006
C	-4.208133	-1.261728	-0.888141
C	-3.847934	0.584300	0.681512
C	-2.301915	0.769704	0.568215
C	-1.986877	1.274424	-0.852764
C	-3.265424	0.867376	-1.623618
H	-4.968533	1.956672	-0.679138
C	-0.960078	-2.179892	-1.546613
H	-4.350182	0.951483	1.561597
H	-1.752365	1.227511	1.369499
H	-1.463359	-1.240087	1.123661
O	-0.989593	0.317558	-1.338736
C	-1.591329	2.734109	-1.056757
H	-3.099001	-1.013707	-2.800435
H	-3.377503	1.376991	-2.569614
C	-3.664479	-0.976261	0.531639
C	-2.119771	-0.772235	0.415716
C	-1.729930	-0.928594	-1.069986
C	-3.084069	-0.680804	-1.773562
H	-4.466852	-2.290978	-1.087148
H	-4.048400	-1.608212	1.316277
C	-0.697271	3.390850	0.012596
H	-2.511813	3.310491	-1.065007
H	-1.163008	2.822341	-2.045859

H	-1.152034	3.219026	0.973128
H	-0.707885	4.469453	-0.156607
Cs	1.544694	-0.055717	0.402000
C	1.436114	3.380021	-1.138439
C	1.384416	3.272719	1.330839
H	-0.059602	-1.844320	-2.039386
H	-1.573363	-2.680264	-2.286423
C	-0.577793	-3.225056	-0.465935
H	-1.260378	-3.170374	0.364551
N	0.815586	-3.036984	0.023637
H	-0.684385	-4.223087	-0.885778
H	2.296848	-4.439391	-0.586388
H	2.135614	-3.378528	1.603638
H	1.504909	4.354571	1.417667
H	2.377844	2.844812	1.309830
C	0.701065	2.813072	2.642798
H	-0.198306	3.377677	2.836464
H	1.401099	3.022337	3.444774
O	0.370335	1.401538	2.624251
C	0.559576	0.646799	3.845521
H	1.615973	0.551948	4.065275
C	-0.058746	-0.744936	3.696305
H	0.071675	1.145466	4.674597
H	-0.025082	-1.234983	4.663040
O	0.685625	-1.514552	2.726124
H	-1.090326	-0.647112	3.387584
C	0.287136	-2.893703	2.542033
H	-0.776774	-2.952400	2.362509
H	0.504224	-3.451531	3.446227
C	1.085942	-3.543035	1.393167
H	0.905635	-4.616701	1.456155
H	0.827950	3.133284	-1.993724
C	2.857296	2.847061	-1.401680
H	1.526975	4.468171	-1.114849
O	2.985729	1.427459	-1.611518
H	3.521583	3.069056	-0.580611
H	3.227634	3.375735	-2.274737
C	2.471503	0.844182	-2.833916
C	3.031509	-0.576386	-2.923626
H	2.813584	1.421837	-3.685198
H	1.390448	0.807461	-2.821406
H	4.057236	-0.555944	-2.579978
H	3.000948	-0.926148	-3.946403
O	2.223504	-1.457686	-2.102170

C	2.869048	-2.572252	-1.449889
C	1.793914	-3.558715	-0.977100
H	3.478270	-2.222152	-0.622593
H	3.518475	-3.092019	-2.145290
H	1.251748	-3.868138	-1.859215
N	0.704086	2.906845	0.066364

HF/ 6-31G// HF/ 3-21G E_h = -9059.3122653 a.u.

Cage-[3.3.1] cryptand (15)

E_h = -1825.68295625 a.u.

H	6.524757	-1.503408	-1.701176
C	5.780220	-0.716346	-1.741677
H	6.116366	0.067378	-2.410702
C	5.392372	-0.186218	-0.343211
C	4.370742	-1.242537	-2.093174
C	4.163395	0.701358	-0.627299
C	3.132947	0.507605	0.515097
C	3.338239	-0.983717	0.869617
C	4.736097	-1.417619	0.322834
H	6.179614	0.285325	0.226287
H	1.904054	-2.459144	-0.108465
H	4.388968	1.738669	-0.827318
C	3.228725	1.539091	1.628577
O	1.860704	0.516095	-0.189922
H	4.220540	-3.198827	-1.017784
H	3.058443	-1.278050	1.866773
C	0.949179	-0.732885	-2.089446
H	5.377902	-2.005531	0.958978
C	4.029936	-2.146014	-0.885064
C	2.639265	-1.703836	-0.329536
C	2.147229	-0.511366	-1.183591
C	3.460329	-0.023726	-1.834191
H	4.258225	-1.703186	-3.063549
H	3.305986	0.618726	-2.688461
H	3.130061	2.522258	1.186328
C	2.230776	1.395889	2.793382
N	0.853448	1.728979	2.432169
H	2.583507	2.023927	3.615284
H	2.250294	0.376308	3.153273
H	4.233362	1.472588	2.038426
H	0.815843	0.123470	-2.739359

H	-0.216030	-1.704352	-0.539695
C	-0.341099	-0.913222	-1.274601
N	-1.512003	-1.153504	-2.123899
H	-0.498673	0.001437	-0.726437
C	-2.780087	-0.660772	-1.562756
C	-1.565849	-2.445596	-2.799414
H	1.145568	-1.598802	-2.712512
H	-0.035261	3.627627	2.767827
C	-0.184287	1.080351	3.234134
H	-1.107834	1.633688	3.134756
H	0.061133	1.043400	4.293896
C	-0.450977	-0.334979	2.733703
O	-1.532225	-0.841269	3.537418
H	0.426083	-0.964768	2.842828
H	-0.710021	-0.293107	1.686988
C	-1.852662	-2.230138	3.389041
C	-1.500455	-3.679809	-1.889830
H	-0.754489	-2.518312	-3.515288
H	-2.490766	-2.486110	-3.358762
O	-2.497090	-3.544040	-0.862032
H	-0.520622	-3.790005	-1.438238
H	-1.689798	-4.566550	-2.489699
C	-2.763140	-4.750043	-0.121175
H	-0.960538	-2.846623	3.421146
C	-2.606424	-2.501933	2.093125
H	-2.485869	-2.495907	4.220537
H	-2.001943	-2.320744	1.220824
H	-3.484742	-1.868922	2.042641
O	-2.978590	-3.892305	2.167103
H	-4.159803	-5.329571	1.393118
H	-3.230028	-5.481470	-0.773812
C	-3.689432	-4.422342	1.040826
H	-1.846411	-5.171125	0.275510
H	-4.452414	-3.735116	0.694824
C	-2.948328	0.812086	-1.907222
H	-2.837191	-0.792774	-0.490286
H	-3.604373	-1.208172	-1.992879
H	-2.160243	1.422235	-1.498736
O	-4.225246	1.200642	-1.354116
H	-2.951816	0.930038	-2.985430
C	-4.683423	2.514060	-1.677570
H	-5.760043	2.497399	-1.569616
H	-4.436694	2.772826	-2.702011
C	-4.111469	3.580119	-0.757317

H	-4.252158	3.291065	0.275827
H	-4.638721	4.512682	-0.937578
O	-2.706129	3.740677	-1.038841
C	-2.171359	5.050351	-0.762600
H	-2.583086	5.761508	-1.472220
C	-0.653862	4.999382	-0.885535
H	-2.420975	5.371774	0.241149
O	-0.025722	4.612661	0.339118
H	-0.278432	5.989080	-1.106802
H	-0.396035	4.331878	-1.699568
C	-0.016224	3.202874	0.662856
C	0.606413	3.122979	2.051940
H	0.592092	2.642203	-0.032086
H	-1.020028	2.802593	0.652857
H	1.535776	3.674200	2.021134

HF/ 6-31G// HF/ 3-21G E_h = -1834.99762220 a.u.

Li^+-cage-[3.3.1] cryptand (15•Li^+)

E_h = -1833.08581246 a.u.

C	6.155580	0.896750	0.705366
C	5.299140	1.131408	-0.558743
C	3.871875	1.283468	0.006914
C	3.724918	-0.617717	-1.452505
H	5.620321	1.925365	-1.215990
C	5.293631	-0.262465	1.252754
H	6.177643	1.755744	1.365286
H	7.169162	0.591767	0.474840
C	3.865261	0.326178	1.254174
H	5.614083	-0.699411	2.186577
C	3.728495	-1.569465	-0.212417
H	3.443857	-2.598752	-0.359019
H	3.431747	-1.023467	-2.407536
C	2.881993	0.576248	-0.947511
C	2.877818	-0.778820	0.809067
H	3.592455	2.298885	0.247671
Li	-1.474032	0.006497	0.004229
C	2.216813	1.458349	-2.000993
H	3.578429	0.819345	2.171939
C	2.200355	-1.588708	1.914859
H	5.939524	-2.045206	0.066623
C	5.230060	-0.274676	-1.197452

H	5.941650	-0.470075	-1.982279
C	5.228814	-1.235749	0.052807
C	0.845787	-1.045504	2.435516
H	2.881340	-1.597044	2.759620
H	2.101612	-2.619994	1.612638
H	0.801027	-1.324161	3.485791
N	-0.421563	-1.538100	1.784933
H	0.828385	0.029991	2.368730
H	2.171521	2.478893	-1.652780
C	0.828098	0.996897	-2.509692
H	2.880271	1.472243	-2.859545
H	0.762152	-0.078960	-2.479280
H	0.772787	1.313055	-3.549189
N	-0.398259	1.523062	-1.811697
C	-0.347431	-2.811124	1.043988
C	-1.503569	-1.554850	2.797286
H	0.398125	3.498004	-1.574379
H	-1.442062	0.709642	-3.424240
H	-1.340192	-3.228764	0.994581
H	0.284561	-3.545963	1.534965
C	0.119507	-2.575003	-0.383594
H	1.056076	-2.062749	-0.417067
O	-0.837302	-1.704577	-1.049178
H	0.188147	-3.519547	-0.912188
C	-1.510546	-2.251358	-2.199015
H	-0.816979	-2.821890	-2.806667
H	-1.847516	-1.405605	-2.762545
C	-2.674620	-3.144148	-1.775751
H	-2.308089	-4.066846	-1.350564
H	-3.289963	-3.389803	-2.635568
O	-3.442723	-2.518235	-0.736075
C	-4.529449	-1.654149	-1.096733
H	-5.320952	-2.229498	-1.567392
C	-4.177237	-0.497957	-2.024174
H	-4.884773	-1.260104	-0.161317
H	-3.904822	-0.854886	-3.010043
O	-3.105205	0.290066	-1.468602
H	-5.067295	0.112417	-2.131239
C	-2.882798	1.574391	-2.126966
H	-2.987045	2.323306	-1.366056
H	-3.640374	1.726640	-2.887797
C	-1.512679	1.579017	-2.786407
H	-1.427830	2.459721	-3.424248
H	-1.429764	-2.439092	3.431514

C	-2.893973	-1.498099	2.184271
H	-1.379922	-0.689644	3.432552
H	-3.051755	-2.243692	1.429344
O	-3.087401	-0.207055	1.530031
H	-3.631081	-1.619836	2.970296
C	-4.106262	0.625537	2.119596
H	-3.786363	0.972018	3.094883
H	-5.017010	0.053114	2.257952
C	-4.440548	1.794468	1.201348
H	-5.192249	2.402086	1.696121
H	-4.842520	1.414731	0.278770
O	-3.332057	2.613314	0.803579
C	-2.504683	3.207502	1.815967
H	-3.080417	3.478240	2.695499
H	-2.115108	4.114301	1.377244
C	-1.364666	2.268334	2.201686
H	-1.717825	1.434205	2.772421
H	-0.631474	2.808873	2.789943
O	-0.747949	1.700402	1.030398
C	0.231595	2.530713	0.346147
H	0.350943	3.470229	0.874721
C	-0.254809	2.790305	-1.070928
H	1.146016	1.978117	0.358974
H	-1.227027	3.251294	-1.000427
O	1.931463	-0.055178	-0.036487

HF/ 6-31G// HF/ 3-21G E_h = -1842.38814784 a.u.

Na^+-cage-[3.3.1] cryptand (15•Na^+)

E_h = -1986.55621326 a.u.

C	6.139512	0.959672	0.629757
C	5.285623	1.085781	-0.651470
C	3.856106	1.274484	-0.102728
C	3.724071	-0.739146	-1.403783
H	5.603661	1.826212	-1.369914
C	5.282721	-0.156776	1.266865
H	6.154334	1.869440	1.217968
H	7.155642	0.643312	0.427439
C	3.850740	0.420997	1.216448
H	5.602812	-0.514855	2.233797
C	3.730543	-1.587701	-0.092307
H	3.454779	-2.627614	-0.156618

H	3.434137	-1.221713	-2.323395
C	2.872988	0.487113	-0.998595
C	2.871982	-0.723175	0.859198
H	3.573385	2.304890	0.055062
Na	-1.359333	0.006961	0.003041
C	2.208186	1.270041	-2.127875
H	3.556601	0.984122	2.090601
C	2.201992	-1.441018	2.029889
H	5.943305	-2.025338	0.230258
C	5.226638	-0.367367	-1.174737
H	5.941341	-0.621291	-1.939731
C	5.227742	-1.224113	0.149284
C	0.850374	-0.850373	2.494861
H	2.883436	-1.372580	2.871441
H	2.104227	-2.495799	1.821835
H	0.808119	-1.017427	3.568013
N	-0.420328	-1.406605	1.903057
H	0.826385	0.211773	2.311704
H	2.174110	2.322231	-1.888770
C	0.813204	0.762982	-2.562879
H	2.860182	1.188592	-2.991227
H	0.735379	-0.299138	-2.393577
H	0.749221	0.948383	-3.632005
N	-0.406684	1.378666	-1.925434
C	-0.365007	-2.753740	1.299312
C	-1.487123	-1.302211	2.932196
H	0.330325	3.388021	-1.944572
H	-1.419281	0.405756	-3.466888
H	-1.374680	-3.127476	1.243575
H	0.206881	-3.453174	1.905473
C	0.195032	-2.731843	-0.123232
H	1.140725	-2.238701	-0.164091
O	-0.666819	-1.963572	-1.000329
H	0.290541	-3.748326	-0.491272
C	-1.425749	-2.665894	-1.995981
H	-0.801522	-3.384613	-2.515985
H	-1.736854	-1.908862	-2.692415
C	-2.628997	-3.380031	-1.388476
H	-2.310505	-4.231887	-0.805759
H	-3.284512	-3.738153	-2.175524
O	-3.322132	-2.509722	-0.477376
C	-4.455242	-1.766842	-0.955322
H	-5.221544	-2.444060	-1.317694
C	-4.137209	-0.753218	-2.045784

H	-4.817086	-1.241614	-0.089034
H	-3.811164	-1.238816	-2.957416
O	-3.125372	0.138260	-1.553387
H	-5.047779	-0.207442	-2.268451
C	-2.900594	1.366607	-2.300805
H	-3.025472	2.169657	-1.599883
H	-3.636662	1.455169	-3.092360
C	-1.510690	1.333030	-2.919059
H	-1.416913	2.149526	-3.635607
H	-1.412795	-2.121679	3.647672
C	-2.896716	-1.263748	2.360289
H	-1.329631	-0.380382	3.474071
H	-3.086277	-2.059948	1.666148
O	-3.082467	-0.026020	1.617387
H	-3.609616	-1.313252	3.176084
C	-4.030077	0.916534	2.141719
H	-3.650015	1.383276	3.042194
H	-4.960059	0.418454	2.394073
C	-4.331370	1.947158	1.062358
H	-5.050551	2.661006	1.450203
H	-4.747724	1.442672	0.208249
O	-3.179407	2.633934	0.547252
C	-2.410296	3.462393	1.435886
H	-3.019242	3.854124	2.244087
H	-2.064819	4.296813	0.843380
C	-1.228514	2.682623	2.003657
H	-1.557170	1.942348	2.709850
H	-0.549670	3.365544	2.503130
O	-0.541682	1.942312	0.983559
C	0.337154	2.663096	0.083375
H	0.499866	3.671744	0.449416
C	-0.261239	2.719578	-1.322502
H	1.254147	2.116580	0.096877
H	-1.246967	3.147834	-1.237284
O	1.919381	-0.075653	-0.043019

HF/ 6-31G// HF/ 3-21G E_h = -199678251752 a.u.

K^+-cage-[3.3.1] cryptand ($15•K^+$)

E_h = -2421.84087359 a.u.

C	-6.711093	-0.702549	-0.424966
C	-5.966648	0.492752	0.210057

C	-4.758477	0.698230	-0.725785
C	-3.772762	0.220047	1.411142
H	-6.556295	1.376592	0.401843
C	-5.476248	-1.628390	-0.487935
H	-7.117695	-0.474582	-1.402977
H	-7.496216	-1.093380	0.211153
C	-4.420700	-0.766676	-1.212711
H	-5.634024	-2.610879	-0.906729
C	-3.437132	-1.227665	0.928743
H	-2.741854	-1.810161	1.512128
H	-3.301107	0.573993	2.312099
C	-3.516598	1.050065	0.133452
C	-3.048679	-1.004438	-0.550347
H	-4.927302	1.386057	-1.541533
K	1.873969	-0.050439	0.095663
C	-3.214987	2.530642	0.276107
H	-4.409627	-0.866996	-2.287807
C	-2.053157	-1.992871	-1.145513
H	-5.263837	-2.422658	1.592848
C	-5.293054	-0.139380	1.449560
H	-5.823212	-0.027287	2.380857
C	-4.953155	-1.602014	0.967513
C	-0.638391	-1.557116	-0.690454
H	-2.110609	-1.989322	-2.228227
H	-2.289783	-2.992574	-0.801464
H	-0.324282	-0.747275	-1.331196
N	0.419865	-2.562218	-0.662895
H	-0.723329	-1.140310	0.302633
H	-3.134210	2.958982	-0.713745
C	-2.004134	2.936390	1.148773
H	-4.087418	2.984508	0.737446
H	-2.010963	2.355774	2.060395
H	-2.169967	3.977482	1.435221
N	-0.636614	2.816834	0.564257
C	0.333287	-3.572498	0.388907
C	1.019702	-2.994043	-1.927435
H	-1.400860	3.982612	-1.040671
H	0.173127	2.900419	2.494190
H	1.032253	-4.365771	0.162293
H	-0.657093	-4.019299	0.453679
C	0.707824	-3.016634	1.762272
H	0.011930	-2.252996	2.090661
O	2.032778	-2.458735	1.659615
H	0.694769	-3.822427	2.488811

C	2.695206	-2.175619	2.907276
H	2.773187	-3.075091	3.506922
H	2.148574	-1.423813	3.466230
C	4.076648	-1.668855	2.540929
H	4.539502	-2.371012	1.866233
H	4.692763	-1.560508	3.425072
O	3.963996	-0.411307	1.837203
C	4.209094	0.779519	2.620438
H	3.629931	0.764142	3.534271
C	3.786799	1.975331	1.792794
H	5.262666	0.844943	2.862019
H	4.170376	2.881962	2.246804
O	2.337532	2.016102	1.778191
H	4.169468	1.878794	0.785500
C	1.804629	3.231725	1.185944
H	1.953369	3.194745	0.120636
H	2.349395	4.074827	1.595994
C	0.323190	3.389039	1.541871
H	0.120054	4.452136	1.679332
H	0.693005	-3.990695	-2.214079
C	2.544080	-2.961621	-1.838582
H	0.723410	-2.308497	-2.709842
H	2.872898	-3.409152	-0.910187
O	2.944477	-1.571087	-1.881336
H	2.989703	-3.489457	-2.674217
C	4.334238	-1.306800	-1.581731
H	4.969353	-2.076347	-2.005737
H	4.481614	-1.259580	-0.511987
C	4.670015	0.025704	-2.217324
H	4.446960	-0.033247	-3.274111
H	5.717727	0.258639	-2.084564
O	3.865353	1.053846	-1.589880
C	3.312702	2.053908	-2.477884
H	3.933682	2.157306	-3.359159
H	3.308106	2.988325	-1.940313
C	1.891153	1.691637	-2.874861
H	1.853178	0.675746	-3.244225
H	1.550514	2.370551	-3.647510
O	1.062442	1.815248	-1.697341
C	-0.287550	2.348212	-1.852593
H	-0.382589	2.788437	-2.839334
C	-0.513651	3.414791	-0.788304
H	-0.998594	1.552254	-1.724215
H	0.312515	4.112778	-0.820300

O	-2.450855	0.329984	-0.538250

HF/ 6-31G// HF/ 3-21G E_h = -2434.07854401 a.u.

Rb^+-cage-[3.3.1] cryptand (15•Rb^+)

E_h = -4750.37805674 a.u.

C	-6.360185	-1.125889	-0.936300
C	-5.782569	0.211377	-0.422478
C	-4.573608	0.454806	-1.349514
C	-3.616969	0.337305	0.849451
H	-6.477010	1.034358	-0.344018
C	-5.023627	-1.897534	-0.868377
H	-6.755587	-1.055367	-1.942499
H	-7.116215	-1.537132	-0.278053
C	-4.052532	-0.995758	-1.660013
H	-5.050174	-2.931156	-1.179430
C	-3.097355	-1.104482	0.538449
H	-2.361399	-1.527873	1.202704
H	-3.211862	0.834518	1.712892
C	-3.417841	1.051481	-0.505337
C	-2.684786	-0.992688	-0.946576
H	-4.792327	1.026765	-2.239451
Rb	2.333875	-0.182878	0.402888
C	-3.346380	2.573303	-0.562511
H	-3.990044	-1.211362	-2.716324
C	-1.613829	-1.947320	-1.452948
H	-4.794069	-2.431980	1.291753
C	-5.084816	-0.197135	0.895287
H	-5.659012	-0.050128	1.795295
C	-4.559081	-1.651898	0.586162
C	-0.241540	-1.537766	-0.887894
H	-1.582741	-1.913543	-2.536587
H	-1.878298	-2.957496	-1.158172
H	-0.017884	-0.554661	-1.267233
N	0.905106	-2.402661	-1.204281
H	-0.306575	-1.449692	0.187738
H	-2.982570	2.841282	-1.546913
C	-2.550968	3.306971	0.532603
H	-4.365844	2.942300	-0.494983
H	-2.909208	2.979825	1.498165
H	-2.791185	4.369877	0.452040
N	-1.089855	3.103578	0.503777

C	0.911465	-3.752468	-0.631451
C	1.353894	-2.377569	-2.606012
H	-1.200622	4.091806	-1.348537
H	-1.058007	3.215499	2.583373
H	1.891277	-4.179328	-0.797576
H	0.184748	-4.406273	-1.115039
C	0.639746	-3.796243	0.868275
H	-0.373354	-3.488492	1.097636
O	1.573981	-2.939131	1.557650
H	0.760098	-4.821033	1.204305
C	1.551391	-3.104304	2.988989
H	1.875559	-4.103150	3.258682
H	0.543297	-2.965875	3.363764
C	2.504033	-2.090670	3.602555
H	3.495527	-2.242384	3.205245
H	2.528585	-2.226638	4.678342
O	2.159196	-0.731135	3.278325
C	0.932149	-0.228281	3.846198
H	0.076605	-0.637172	3.326017
C	0.940488	1.277881	3.685933
H	0.870575	-0.484006	4.898545
H	0.064919	1.695521	4.169114
O	0.942036	1.562565	2.278158
H	1.829945	1.684075	4.151686
C	0.959634	2.967528	1.922342
H	1.489261	3.015128	0.991188
H	1.496205	3.527195	2.681949
C	-0.445022	3.541061	1.753621
H	-0.377841	4.629936	1.804350
H	0.988576	-3.239821	-3.160383
C	2.874924	-2.314247	-2.709756
H	0.968788	-1.486208	-3.081262
H	3.343493	-3.064144	-2.084178
O	3.267276	-0.991052	-2.289798
H	3.182524	-2.477957	-3.737056
C	4.669206	-0.677663	-2.381923
H	5.091896	-1.073872	-3.298554
H	5.207861	-1.090440	-1.537388
C	4.778645	0.834269	-2.393060
H	4.175883	1.209918	-3.207462
H	5.807781	1.140160	-2.537246
O	4.291922	1.319716	-1.126075
C	3.964424	2.722249	-1.070386
H	4.749849	3.317105	-1.523516

H	3.906241	2.965985	-0.020733
C	2.631946	3.036328	-1.739769
H	2.652631	2.788599	-2.793344
H	2.443649	4.100220	-1.646974
O	1.605198	2.270344	-1.081344
C	0.243888	2.533398	-1.538222
H	0.280312	2.807862	-2.587392
C	-0.446523	3.630552	-0.722482
H	-0.319469	1.627311	-1.417451
H	0.265322	4.413133	-0.475577
O	-2.240791	0.394856	-1.066156

HF/ 6-31G// HF/ 3-21G E_h = -4759.6727576 a.u.

Cs^+-cage-[3.3.1] cryptand (15•Cs^+)

E_h = -9355.73592623 a.u.

C	-6.356737	-0.967379	-1.260098
C	-5.787929	0.341219	-0.668605
C	-4.556785	0.624128	-1.554667
C	-3.652512	0.397962	0.657919
H	-6.481720	1.162192	-0.566646
C	-5.023857	-1.746007	-1.198671
H	-6.728108	-0.846535	-2.270657
H	-7.129050	-1.407527	-0.640524
C	-4.032331	-0.809874	-1.922481
H	-5.045669	-2.763220	-1.560193
C	-3.129738	-1.029371	0.289144
H	-2.411072	-1.485959	0.949851
H	-3.261387	0.851974	1.550891
C	-3.421402	1.176322	-0.655343
C	-2.681073	-0.845924	-1.178467
H	-4.753152	1.239579	-2.420435
Cs	2.460692	-0.304606	0.637841
C	-3.352552	2.700970	-0.642404
H	-3.945397	-0.974682	-2.986218
C	-1.610242	-1.783302	-1.715951
H	-4.847279	-2.385664	0.937498
C	-5.122531	-0.132983	0.644156
H	-5.718153	-0.027990	1.536164
C	-4.593328	-1.572947	0.276556
C	-0.253889	-1.482176	-1.052246
H	-1.526309	-1.648715	-2.788784

H	-1.920317	-2.807068	-1.532666
H	0.020450	-0.475285	-1.320940
N	0.876515	-2.354811	-1.404344
H	-0.359996	-1.506383	0.021688
H	-2.902306	3.006463	-1.578938
C	-2.659689	3.388649	0.547397
H	-4.374723	3.068120	-0.651745
H	-3.113314	3.035800	1.462831
H	-2.878042	4.456986	0.480425
N	-1.208674	3.154607	0.642999
C	0.843117	-3.746864	-0.938817
C	1.373212	-2.231341	-2.783722
H	-1.129529	4.223779	-1.160402
H	-1.364362	3.151972	2.719070
H	1.854637	-4.132416	-0.953284
H	0.246719	-4.378181	-1.599293
C	0.289466	-3.938530	0.469917
H	-0.758930	-3.671319	0.516913
O	1.035970	-3.143580	1.414755
H	0.375531	-4.989727	0.726262
C	0.640115	-3.376453	2.780753
H	0.782638	-4.420094	3.039918
H	-0.410475	-3.141187	2.909291
C	1.507561	-2.526387	3.696274
H	2.545957	-2.760410	3.519075
H	1.265881	-2.758237	4.728292
O	1.377731	-1.114318	3.459189
C	0.122463	-0.512526	3.834197
H	-0.656424	-0.778411	3.133361
C	0.309654	0.991611	3.816805
H	-0.164341	-0.833885	4.830044
H	-0.584233	1.465259	4.205873
O	0.554004	1.381065	2.457612
H	1.150416	1.257275	4.445971
C	0.688049	2.803504	2.219973
H	1.307525	2.886606	1.346324
H	1.180810	3.272243	3.066307
C	-0.658439	3.480195	1.967756
H	-0.527937	4.556879	2.092470
H	1.032391	-3.058811	-3.403198
C	2.896868	-2.148181	-2.848925
H	0.995216	-1.314649	-3.213796
H	3.361923	-2.918068	-2.245149
O	3.264682	-0.836354	-2.375101

H	3.225248	-2.270915	-3.875942
C	4.634414	-0.438104	-2.561694
H	4.992191	-0.746365	-3.538110
H	5.271688	-0.872634	-1.801313
C	4.667370	1.075922	-2.472500
H	3.947240	1.468261	-3.175727
H	5.653706	1.447342	-2.724953
O	4.330599	1.446217	-1.122208
C	4.050151	2.840294	-0.895079
H	4.821055	3.462995	-1.336390
H	4.070139	2.971466	0.176236
C	2.687260	3.261965	-1.429997
H	2.633560	3.128670	-2.503269
H	2.542760	4.315155	-1.216337
O	1.681199	2.458323	-0.788604
C	0.321541	2.657778	-1.278427
H	0.373575	2.927119	-2.327974
C	-0.442445	3.726513	-0.487273
H	-0.207237	1.729522	-1.170738
H	0.248424	4.488110	-0.136615
O	-2.230151	0.544047	-1.218053

HF/ 6-31G// HF/ 3-21G E_h = -9365.04062230 a.u.

APPENDIX C

CARTESIAN COORDINATES AND ENERGIES OBTAINED FROM GEOMETRY OPTIMIZATIONS OF ALKALI METAL PICRATE COMPLEXED **31**

Cartesian (x, y, z) coordinates and energies corresponding to stationary points obtained from geometry optimizations at the B3LYP level of theory with 6-31G basis set.

Na^+ picrate complexed 31

E_h = -2701.78290873 a.u.

Na	0.314519	-1.042013	-0.065147
N	0.007935	3.571517	1.478222
N	-4.203646	5.310619	-0.221325
N	-2.736806	0.960474	-1.819965
O	2.801291	-0.561749	-0.190643
O	1.155472	-0.774907	-2.441065
O	-0.360864	-3.052199	-1.718069
O	-2.141757	-2.031108	0.129446
O	-0.809964	-1.140825	2.350167
O	1.909131	-1.321128	2.427136
O	-0.541239	1.095056	0.019422
O	-1.752252	0.411961	-2.400007
O	-3.938285	0.573859	-1.983375
O	-5.229546	5.164370	-0.956169
O	-3.988666	6.340682	0.488088
O	-0.070504	4.468943	2.376912
O	1.054754	2.876993	1.296553
C	3.344667	0.561046	-1.007030
C	2.229585	1.287041	-1.740344
H	1.465022	1.550936	-1.003587
H	2.632263	2.231028	-2.135231
C	1.590369	0.538297	-2.903906
H	0.724149	1.096856	-3.281134
H	2.304509	0.399008	-3.730689
C	0.638981	-1.635470	-3.485461
H	1.342339	-1.672347	-4.332634
H	-0.321303	-1.250003	-3.850389
C	0.511849	-3.024795	-2.883100
H	0.151362	-3.736117	-3.641754
H	1.484694	-3.355819	-2.513411
C	-1.781004	-2.919055	-2.044217
H	-2.056904	-3.687432	-2.782404
H	-1.980522	-1.924905	-2.455329
C	-2.604542	-3.108609	-0.782280
C	-2.850757	-2.008623	1.434272
C	-2.220970	-0.846836	2.188301
H	-2.353055	0.081527	1.621795

H	-2.700327	-0.740140	3.173629
C	-0.057591	-0.208834	3.179589
H	-0.650162	0.086285	4.058221
H	0.201312	0.680116	2.594113
C	1.188442	-0.940047	3.625145
H	1.806903	-0.279653	4.252605
H	0.920033	-1.833671	4.207426
C	3.189556	-1.956107	2.669372
H	3.045615	-2.903718	3.211787
H	3.813475	-1.302130	3.298077
C	3.855295	-2.216800	1.323872
H	3.258190	-2.942856	0.757628
H	4.830119	-2.686570	1.516211
C	4.070622	-0.994184	0.443189
C	4.508043	-0.107939	-1.794150
H	4.271365	-0.429238	-2.808428
C	5.805391	0.735635	-1.544734
H	6.442183	0.978755	-2.397037
C	5.434212	1.931288	-0.614670
H	5.353767	2.901390	-1.111121
C	4.122015	1.415098	0.041268
H	3.501120	2.180170	0.510710
C	5.015885	-1.195867	-0.781130
H	5.099363	-2.226737	-1.130304
C	6.318249	-0.363783	-0.526696
H	7.283984	-0.832219	-0.723980
C	6.180985	0.342247	0.857124
H	6.766578	-0.100868	1.667096
C	4.639121	0.316846	1.063048
H	4.307949	0.508227	2.084423
C	6.478639	1.827218	0.526031
H	7.507487	1.992911	0.183672
H	6.272264	2.505305	1.361862
C	-2.384014	-4.468885	-0.094717
H	-2.724160	-5.270808	-0.764234
H	-1.313539	-4.611865	0.083111
C	-3.174169	-4.499769	1.235417
H	-3.022126	-5.466769	1.731684
C	-4.683045	-4.279407	0.960824
H	-5.074343	-5.086357	0.325909
H	-5.244911	-4.309628	1.904675
C	-4.887689	-2.911976	0.262332
H	-5.953682	-2.746920	0.063745
C	-4.105199	-2.887292	-1.072930

H	-4.470004	-3.677990	-1.742367
H	-4.240881	-1.923884	-1.577220
C	-2.639985	-3.364484	2.138650
H	-1.573732	-3.495792	2.343139
H	-3.170225	-3.356314	3.100967
C	-4.350436	-1.771439	1.162595
H	-4.485308	-0.804772	0.662448
H	-4.898616	-1.742423	2.113749
C	-1.301701	2.105607	-0.111220
C	-1.146822	3.355450	0.629207
C	-2.087677	4.372231	0.599686
H	-1.934238	5.263877	1.192522
C	-3.231279	4.243483	-0.190996
C	-3.441422	3.099200	-0.968307
H	-4.328996	3.013695	-1.581350
C	-2.493886	2.094870	-0.958649

K^+ picrate complexed 31

E_h = -3139.39038512 a.u.

K	0.085573	-1.399046	-0.004051
N	0.907049	3.682250	1.623187
N	-2.686135	6.115303	-0.569711
N	-2.106897	1.436629	-1.729554
O	2.759593	-1.353156	-0.408430
O	0.943086	-1.678137	-2.687197
O	-1.367241	-3.159248	-1.729556
O	-2.700073	-1.611069	0.222090
O	-1.158007	-1.178653	2.566806
O	1.658831	-1.722915	2.442639
O	0.027424	1.282902	0.206552
O	-1.263993	0.550719	-2.077722
O	-3.330647	1.385798	-2.080752
O	-3.661224	6.129395	-1.383724
O	-2.307931	7.131062	0.090784
O	1.443957	4.813683	1.848046
O	1.303140	2.615923	2.183643
C	3.351070	-0.282284	-1.249318
C	2.336610	0.286729	-2.230303
H	1.500878	0.715274	-1.666160
H	2.822602	1.123638	-2.753555
C	1.771688	-0.643077	-3.300423
H	1.148975	-0.048572	-3.984277

H	2.566582	-1.123601	-3.890395
C	0.038203	-2.326094	-3.617981
H	0.589119	-2.696932	-4.497179
H	-0.715136	-1.603962	-3.962437
C	-0.599628	-3.513696	-2.912990
H	-1.237735	-4.060814	-3.624492
H	0.181808	-4.184787	-2.548062
C	-2.653063	-2.514393	-1.993685
H	-3.201101	-3.093609	-2.752652
H	-2.495889	-1.492503	-2.352995
C	-3.472345	-2.475802	-0.709903
C	-3.349172	-1.411694	1.543641
C	-2.410990	-0.489460	2.311509
H	-2.226942	0.417434	1.720729
H	-2.879823	-0.202591	3.265577
C	-0.170530	-0.372253	3.280218
H	-0.617768	0.034890	4.200382
H	0.170918	0.457842	2.650349
C	0.982672	-1.274174	3.653879
H	1.687660	-0.709461	4.282413
H	0.621122	-2.143917	4.220806
C	2.920391	-2.395070	2.719119
H	2.732264	-3.303609	3.312070
H	3.555876	-1.728566	3.322182
C	3.621916	-2.767201	1.416603
H	3.025321	-3.509442	0.871369
H	4.563284	-3.262139	1.694146
C	3.932496	-1.624091	0.455981
C	4.663835	-0.934517	-1.775072
H	4.610357	-1.370680	-2.773263
C	5.850475	0.028994	-1.425754
H	6.597829	0.235665	-2.193698
C	5.265764	1.278932	-0.699022
H	5.207278	2.186682	-1.304523
C	3.901313	0.729525	-0.197051
H	3.167042	1.480648	0.099349
C	5.070319	-1.875554	-0.583339
H	5.269968	-2.926107	-0.802070
C	6.263106	-0.922549	-0.228605
H	7.274854	-1.331545	-0.227383
C	5.866785	-0.096003	1.032623
H	6.343457	-0.409867	1.965183
C	4.317299	-0.219694	1.006097
H	3.813932	0.050236	1.934408

C	6.121098	1.368107	0.591194
H	7.178784	1.578998	0.391655
H	5.742860	2.105994	1.307319
C	-3.657956	-3.857389	-0.053841
H	-4.235733	-4.503695	-0.728840
H	-2.676859	-4.319293	0.092435
C	-4.396457	-3.687235	1.295032
H	-4.530928	-4.669347	1.765991
C	-5.776332	-3.023563	1.058282
H	-6.397880	-3.662697	0.416121
H	-6.308620	-2.909674	2.012818
C	-5.577723	-1.638826	0.392038
H	-6.550518	-1.161907	0.220562
C	-4.842362	-1.807114	-0.959464
H	-5.437324	-2.429611	-1.641166
H	-4.688334	-0.832117	-1.436100
C	-3.537098	-2.787081	2.213723
H	-2.554792	-3.233174	2.393909
H	-4.026865	-2.652270	3.187829
C	-4.716472	-0.735290	1.307247
H	-4.563334	0.242622	0.834138
H	-5.219819	-0.571895	2.269407
C	-0.554593	2.394022	0.006359
C	-0.208310	3.637737	0.694068
C	-0.879702	4.829414	0.489489
H	-0.563015	5.723808	1.009009
C	-1.970512	4.874743	-0.384869
C	-2.371562	3.738677	-1.090561
H	-3.215191	3.787941	-1.766099
C	-1.668312	2.557036	-0.933374

APPENDIX D

CARTESIAN COORDINATES OF THE X-RAY CRYSTAL STRUCTURES USED IN COMPUTATIONAL STUDIES

Na^+-cage-[2.2.1] cryptand ($9•Na^+$)[45]

H	9.140719	6.727608	2.939415
C	8.556156	6.111504	3.359228
H	8.922454	5.834928	4.189074
C	7.119657	6.647112	3.493250
C	8.209221	4.944312	2.466356
C	6.702314	6.791592	2.024266
C	5.361041	6.048552	1.839534
C	4.984182	5.429352	3.212167
C	6.330911	5.398392	3.911433
H	7.012637	7.415952	4.044186
C	6.068642	2.374632	1.691024
H	6.776770	7.701816	1.753145
H	4.615244	6.501600	1.463369
H	5.833303	4.552152	0.302454
O	4.760285	4.032850	2.880373
C	3.834948	6.007272	3.962143
H	7.378758	3.561432	3.763466
O	3.994774	2.296097	5.680334
H	6.248710	5.330280	4.851937
C	7.441598	5.646072	1.339671
C	6.080963	4.892712	1.156750
C	6.022876	3.757512	2.214432
C	7.054354	4.263192	3.212167
H	8.934775	4.381872	2.220409
H	8.028272	5.771976	0.603096
C	2.514798	6.151752	3.225026
H	4.090705	6.873120	4.252463
H	3.678818	5.449992	4.714293
H	2.034791	6.875184	3.605900
H	2.696626	6.339576	2.310964
Na	2.989348	2.654820	3.390923
C	0.847888	5.006232	4.518151
C	0.802123	4.841112	2.073166
H	6.824295	2.305488	1.119260
H	5.275319	2.229120	1.182648
C	6.167389	1.249752	2.709043
H	6.572587	0.505680	2.281986
N	4.885611	0.795672	3.295296
H	6.720444	1.552128	3.417546
H	5.914272	-0.130032	4.732404
H	4.838790	-1.046448	2.553651
H	0.503417	5.710056	1.836455

H	0.051046	4.294152	2.278364
C	1.499338	4.252872	0.906999
H	0.899462	4.232232	0.166621
H	2.247775	4.794672	0.690029
O	1.958046	2.903842	1.177939
C	0.872531	1.982472	1.124150
H	0.258749	2.148624	1.829211
C	1.462374	0.651192	1.274652
H	0.418928	2.046456	0.287965
H	0.781529	-0.010320	1.177215
O	2.053097	0.530242	2.550753
H	2.122801	0.518064	0.604907
C	2.882680	-0.599592	2.712484
H	2.599815	-1.272456	2.106309
H	2.803999	-0.910224	3.602278
C	4.324459	-0.260064	2.435567
H	4.389939	0.029928	1.530380
H	0.123214	5.601696	4.379240
C	0.303987	3.664632	4.880371
H	1.390558	5.314800	5.228646
O	1.303252	2.691353	5.144248
H	-0.234107	3.760608	5.654254
H	-0.234107	3.354000	4.156476
C	1.832016	2.767824	6.446973
C	2.969105	1.848312	6.557631
H	1.161732	2.521176	7.074157
H	2.121041	3.653280	6.619571
H	3.289814	1.839024	7.449054
H	2.694866	0.970080	6.308061
C	5.135912	1.477824	5.655703
C	5.093667	0.342624	4.686765
H	5.255957	1.117656	6.523582
H	5.879068	2.025816	5.431489
H	4.377617	-0.238392	4.924381
N	1.660749	4.944312	3.284430

K^+ picrate complexed 31[80]

K	0.112794	-1.564858	0.082375
N	0.973154	3.636458	1.548002
N	-2.604146	6.023962	-0.711067
N	-2.000775	1.336698	-1.810172
O	2.773482	-1.452299	-0.386848

O	0.919341	-1.985516	-2.617503
O	-1.437054	-3.297664	-1.542767
O	-2.703177	-1.534797	0.257736
O	-1.175464	-1.027733	2.576370
O	1.658987	-1.649934	2.519752
O	0.138258	1.219396	0.125396
O	-1.171615	0.420904	-2.111128
O	-3.221115	1.294287	-2.181243
O	-3.572418	6.024197	-1.533603
O	-2.245080	7.045734	-0.049239
O	1.464116	4.780691	1.816827
O	1.414300	2.568529	2.075261
C	3.324218	-0.409760	-1.292131
C	2.313526	0.011085	-2.348455
H	1.445825	0.465382	-1.856968
H	2.783790	0.803581	-2.950136
C	1.810521	-1.059348	-3.314162
H	1.251035	-0.569011	-4.124199
H	2.634756	-1.631668	-3.764744
C	0.007978	-2.698037	-3.491592
H	0.556247	-3.174707	-4.320752
H	-0.717658	-1.993371	-3.922714
C	-0.672110	-3.789660	-2.677663
H	-1.320531	-4.389315	-3.335606
H	0.087547	-4.440828	-2.236956
C	-2.673182	-2.595132	-1.885248
H	-3.240075	-3.192900	-2.616104
H	-2.444702	-1.613042	-2.311575
C	-3.517633	-2.408752	-0.630850
C	-3.370588	-1.187622	1.539844
C	-2.382264	-0.281713	2.263240
H	-2.135795	0.573704	1.620805
H	-2.840782	0.093080	3.192366
C	-0.165031	-0.241138	3.282824
H	-0.611586	0.209635	4.183265
H	0.220424	0.555718	2.634710
C	0.947421	-1.174763	3.701710
H	1.644279	-0.626664	4.353982
H	0.540516	-2.030912	4.258627
C	2.948335	-2.246413	2.837952
H	2.799757	-3.122858	3.488692
H	3.550126	-1.513568	3.397696
C	3.673884	-2.668484	1.563312
H	3.120020	-3.476554	1.067427

H	4.636380	-3.097265	1.879495
C	3.937149	-1.580192	0.526837
C	4.691172	-1.014559	-1.731068
H	4.694797	-1.525371	-2.695183
C	5.804814	0.047036	-1.428259
H	6.551557	0.249856	-2.198434
C	5.120738	1.308837	-0.814519
H	5.026201	2.163109	-1.490203
C	3.778530	0.712129	-0.308358
H	2.991005	1.433325	-0.082775
C	5.118452	-1.836500	-0.462188
H	5.387707	-2.886635	-0.593040
C	6.239677	-0.785824	-0.150627
H	7.270323	-1.137662	-0.075246
C	5.753758	0.107984	1.032621
H	6.219465	-0.104900	1.999197
C	4.216735	-0.117467	0.975609
H	3.667668	0.191412	1.865496
C	5.929209	1.548525	0.486950
H	6.977344	1.813909	0.299788
H	5.482049	2.310973	1.135270
C	-3.823651	-3.719000	0.120160
H	-4.433600	-4.370048	-0.521853
H	-2.884790	-4.242819	0.328795
C	-4.580731	-3.392434	1.430850
H	-4.796815	-4.324542	1.969252
C	-5.901468	-2.644181	1.100218
H	-6.557746	-3.280117	0.489661
H	-6.449362	-2.415025	2.025225
C	-5.581942	-1.334040	0.338129
H	-6.511026	-0.800097	0.100384
C	-4.825897	-1.659821	-0.971535
H	-5.449496	-2.287829	-1.622620
H	-4.587026	-0.737396	-1.513505
C	-3.676425	-2.491001	2.303679
H	-2.733647	-2.993129	2.543227
H	-4.176241	-2.246952	3.251876
C	-4.676368	-0.430572	1.209151
H	-4.437364	0.493667	0.667747
H	-5.191758	-0.155249	2.139303
C	-0.451357	2.322462	-0.086210
C	-0.117721	3.575208	0.594128
C	-0.799861	4.759385	0.373404
H	-0.496415	5.658694	0.892690

C	-1.879213	4.790815	-0.512503
C	-2.269035	3.645438	-1.210022
H	-3.109933	3.683141	-1.890187
C	-1.563924	2.468734	-1.033014

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